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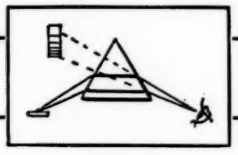

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A Photometric Comparison of Absorption Lines

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(Received January 21, 1937)

A LARGE amount of work has been done in recent years in investigating the intensities of *emission* lines. The photometric methods have been reported in this journal by Harrison.[1] Little quantitative work has been published, however, on the intensities of sharp *absorption* lines for their investigation involves great experimental difficulty. Only for faint absorption can the intensity be well determined, since for intense absorption the intensity transmitted descends very nearly to zero. Faint and sharp absorption lines appear on the photographic plate exceedingly narrow, possibly with a width of 1/100 mm. Thus they are very difficult to measure with the densitometer. They require very high resolving power, as for example, the second order of a 21-foot grating. It is impossible to widen these absorption lines, as can be done with emission lines, by applying a broad slit without causing their disappearance.[2]

Yet for intensity measurements absorption has various definite advantages over emission, for in most cases the absorption coefficient is proportional to the concentration of the absorbing molecules (Beer's law), whereas the intensity of emission lines is very largely determined by uncontrollable factors. Practically absorption alone offers a chance for quantitative chemical analysis of a gas.

This is of importance in the following chemical problem: In theories of reactions in gases, radicals, such as hydroxyl, play a predominant part although no characteristic chemical test exists for most radicals. But some radicals show clear absorption spectra. Absorption spectra of hydroxyl radicals have been photographed during the progress of certain gas reactions.[3] Because the concentration of OH varies rapidly, due to its strong reactivity, the absorption spectra have been taken in snapshots.

While *qualitative* analysis is comparatively simple, for *quantitative* analysis intensities of absorption lines must be measured. The photometric problem is simplified if the aim is to determine solely the *relative* concentrations responsible for two observed absorption spectra. The rotational structure of the band serves for this purpose. On one exposure of an absorption spectrum the lines of any branch of the band indicate relative concentrations of the various rotational quanta. These concentrations can be computed from the Boltzmann formula provided

[1] G. R. Harrison, J. Opt. Soc. Am. **24**, 59 (1934).
[2] Cf. W. H. J. Childs and R. Mecke, Zeits. f. Physik **68**, 353 (1931).
[3] A. A. Frost and O. Oldenberg, J. Chem. Phys. **4**, 643 (1936).

that the temperature is known. Hence, instead of the conventional *intensity marks* of photographic photometry, these lines directly give *concentration marks* which are much more valuable for chemical analysis. For example, the lines with the rotational quantum numbers 3 and 5 may represent concentrations with the ratio 8 : 15. Suppose that on a later exposure the absorption spectrum is weaker so that the line with rotational quantum number 5 has only the intensity of the line 3 on the first exposure. We conclude that the concentrations indicated by the two absorption spectra are in the ratio 8 : 15.[4] Thus the chemical problem of determining relative concentrations of radicals is transformed to the optical problem of selecting absorption lines of equal intensities from two spectra.

This problem is solved by the apparatus shown in Fig. 1. One of the two spectra, *S*, to be compared is mounted on an adjustable holder. The microscope objective, *O*, with its optical axis horizontal forms the image. The right half of Fig. 1 shows the same arrangement for the other spectrum. The distances are so adjusted that both images would coincide at the middle of the optical axis except for the effect of the reflecting prism, *P*. Its two planes forming a right angle are coated with aluminum by the evaporation method.[5] Its edge is mounted exactly in the optical axis so that the lower half of the left image is turned into a horizontal plane (indicated by an arrow). It appears on the left side of the edge and adjoins the half-image of the right spectrum which is formed correspondingly in the right half of the instrument. (The other halves of the images are not observed.) In this way two

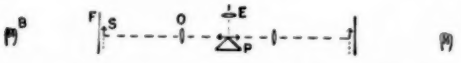

FIG. 1. Microscope for matching absorption lines. *B*, electric light bulb; *F*, frosted glass; *S*, spectral plate; *O*, objective; *P*, prism with two reflecting sides; *E* eyepiece.

spectra, photographed on two plates, or on one plate, afterwards cut for this investigation, can be compared. Plates of frosted glass, *F*, in back

[4] Actually a correction must be applied due to the fact that the probabilities of transition depend on the quantum numbers. This correction is given by the theory of Hill and Van Vleck. Phys. Rev. **32**, 250 (1928).

[5] We are obliged to Dr. H. M. O'Bryan for the aluminum coating of the prism.

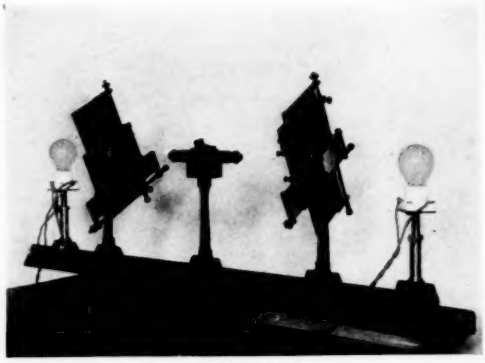

FIG. 2. Microscope for matching absorption lines.

of the spectral plates provide for uniform illumination.

Absorption lines of equal intensity cannot be selected from the two spectra compared unless the two backgrounds appear to the observer with the same intensity. In case their densities are not exactly equal the denser background must be more intensely illuminated. This is done by adjusting the distances of the two bulbs illuminating the plates. Such a compensation is admissible if all densities of backgrounds and absorption lines lie within the linear range of the characteristic curve of the photographic plate. This is practically true in all photographs of absorption spectra.

Fig. 2 shows the finished apparatus, as it was built at the shop of the research laboratory of physics of Harvard University. The fine adjustment of the plateholders permits a smooth shifting of the spectral plates in any direction.

It is important that the edge of the prism is exactly in the common optical axis of both objectives so that a common exit pupil results. If, instead, the two objectives would form two exit pupils, not completely coinciding, the intensities observed would depend on the position of the eye so that no comparative photometric work could be done. In order to prevent this error it was found advisable to mount the prism so that it is adjustable in the proper direction. The objectives are a matched pair of 50 mm focus, the eyepiece is a $12\frac{1}{2}\times$ Ramsden (positive) eyepiece, all taken from the binocular microscope of the Spencer Lens Company.

The photometric procedure is simple. The backgrounds are kept equally dark by adjusting the distances of the bulbs. By shifting the two spectra with respect to each other, absorption lines of equal intensity are found. The eye is well capable of selecting such pairs or of interpolating between them.

The instrument described proved useful in the analysis of the hydroxyl reactions discussed in a recent paper.

If the photometer described is not available, the two absorption spectra to be matched may be enlarged, and the enlargements cut in such a way that they can be compared side by side under a magnifying lens. Again one may compensate in the enlargement for a slight inequality of the backgrounds of the two original absorption spectra. A detailed analysis shows that such a procedure is admissible. The only condition is that all densities of the *original* spectra are restricted to the linear range of the characteristic curve. No assumption is made regarding the characteristic curve of the enlargement plate. In particular, it is not assumed that the original or the enlargement plate are fogged to the beginning of the linear range although this procedure may be advisable for the original spectra in order to reduce the time of exposure.

The instrument described obviously serves equally well for matching *emission* lines. This problem is simpler as the background does not introduce an inequality. But the main purpose of the procedure described is the investigation of the intensities of *absorption* lines belonging to a molecular band for the purpose of quantitative chemical analysis.

A Direct Reading Comparator for Spectra

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(Received January 8, 1937)

An instrument is described which, by the addition of two moving parts to the conventional form of comparator, enables the observer to read from the precision screw directly the values of the wave-lengths or wave numbers that would ordinarily be computed by the Hartmann formula. The extra moving parts are (1) a light carriage on geometric ball bearing ways to carry the plate and (2) a transfer mechanism functioning between that and the main carriage. The whole apparatus operates on a principle of geometric projection and is, in effect, a mechanical equivalent of the Hartmann formula. It is applicable to grating as well as prismatic spectra.

INTRODUCTION

THE task of evaluating spectrograms, especially when many lines have been photographed on a single plate, has long been recognized as needlessly tedious. For, from time to time, there have appeared descriptions of labor-saving devices applying either to the operation of the conventional comparator itself or to the computation of wave-lengths or wave numbers from the measured positions of the lines.

Thus Kayser[1] in 1900 and Lohse[2] in 1910 proposed attachments for recording intensities and micrometer readings, relieving eye strain and saving time in running a plate through the comparator. Short cuts to computation are found in the proposals of King,[3] Henroteau,[4] and Grassmann,[5] who applied a principle of geometric projection as the equivalent of the Cornu-Hartmann hyperbolic interpolation formula (called hereafter the Hartmann formula) particularly for prismatic spectra. King realized the projection optically by photographing the spectrum plate at such an orientation and position with respect to the camera that the second plate could afterwards be measured on a conventional type comparator as a nearly normal spectrum. Henroteau and Grassmann used graphical methods. Conrad-Billroth[6] shortened the computations by measuring the plate relative to a curve drawn to correct for prismatic dispersion.

The recent machine of Harrison[7] is in a class by itself. Without relying upon extended eye observations, it automatically produces a photographic record of both the wave-length values and the plate densities of the lines. It is, necessarily, elaborate, employing photoelectric cells, tube circuits, gear trains, photographic film apparatus, etc. In the opinion of the authors a field is still open for simpler apparatus, especially for those unable to afford and maintain such equipment or where plates need be measured but occasionally.

An operator, using the instrument here described, observes a spectrogram through a microscope in the usual manner but the settings he makes are read off directly in wave-lengths or wave numbers without the necessity of making any computation. It has been estimated by Harrison[7] that the time required for making this computation is on the average at least double that required for making the settings.

The principle already referred to of geometric projection as a substitute for the Hartmann formula is employed. The unique feature, however, is that the projection is realized mechanically on the comparator itself and yields by direct reading results that are good insofar as the Hartmann formula is good, the errors of the added mechanism being negligible as compared with the errors of setting. It differs from the in-

[1] H. Kayser, *Handbuch der Spectroscopie*, Vol. I, p. 644.
[2] O. Lohse, Zeits. f. Inst. **30**, 169 (1910).
[3] E. S. King, Ann. Harv. Coll. Obs. **59**, 205 (1912).
[4] F. Henroteau, M. N., Roy. Astron. Soc. **77**, 77 (1916–17).
[5] P. Grassmann, Physik. Zeits. **32**, 149 (1931).
[6] H. Conrad-Billroth, Zeits. f. Inst. **54**, 301 (1934).
[7] G. R. Harrison, J. Opt. Soc. Am. **25**, 169 (1935).

struments of Conrad-Billroth[6] and Harrison[7] in that no specially constructed set of dispersion curves or templates is required.

Theory

The Hartmann formula, as usually written

$$(\lambda-\lambda_0)(s-s_0)=K, \tag{1}$$

may be thrown into the form

$$A\lambda s+B\lambda+Cs+1=0, \tag{2}$$

where λ is the wave-length, s the conventional comparator reading, and the other letters are disposable constants. On the other hand, when wave numbers are substituted as reciprocals of λ, we get

$$A'\nu s+B'\nu+C's+1=0, \tag{3}$$

an equation of the same form with different constants. The Hartmann formula and its mechanical equivalent to be described, therefore, apply equally well to wave-lengths and wave numbers. In order to be brief, the following discussion will be given in terms of wave-lengths only. Incidentally, it appears that if $A=0$, Eq. (2) will apply to the special case of normal spectra.

A projective graphical representation of the Hartmann formula is shown in Fig. 1. The readings s are laid off on an "s scale" and the corresponding values of λ, by proportional measure, are laid off on a "λ scale." The two scales are inclined at some angle, say, D. P is a fixed point through which any point s on the s scale will be brought into projection with some one point on the λ scale by the straight line λPs. By drawing the construction lines Ps_0 and $P\lambda_0$ through P parallel to the λ scale and s scale, respectively, and intersecting them at s_0 and λ_0, we get two triangles from whose similarity it follows that the product of the segments ss_0 and $\lambda\lambda_0$ is a constant or, translating into scale readings, $(\lambda-\lambda_0)(s-s_0)$ is a constant.

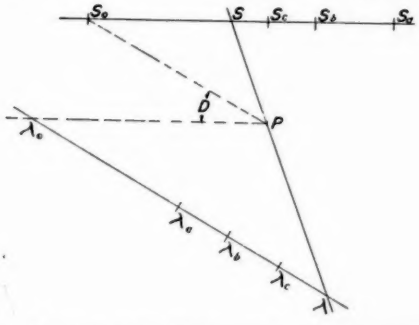

FIG. 1. Solution of the Hartmann formula by geometric projection.

If the positions of P and the two scales are so chosen that three given points s_a, s_b and s_c are brought into projection with the corresponding given points λ_a, λ_b and λ_c, the result is the geometrical counterpart of the analytical solution for the three disposable constants of the Hartmann formula. Then any point s will be projected into a point λ in accordance with the formula as solved for a given plate in terms of three known lines. The number of geometrical solutions is infinite, of which some, fortunately, are to be found that are adaptable to a mechanical design.

Fig. 2 shows an equivalent construction in which the two scales are parallel and, instead of a straight line passing through P, there are two lines intersecting at P at a fixed angle which is equal to the angle D of Fig. 1. This arrangement lends itself more readily to mechanical design and to convenience in operation. Fig. 2, in fact, may be considered as a schematic diagram of the comparator, the plate itself taking the place of the s scale and the precision screw the λ scale. The screw would then read off wave-lengths according to the Hartmann formula.

Description

The mechanical principle for realizing the projection is shown in Fig. 3. Two straight edges are capable of turning about a pivot as a single rigid unit and the angle between them is equal to D. The lines joining the centers of the balls with the center of the pivot determine the projection lines. Both the straight edges and the balls are made of hardened steel. The principle was tested for pre-

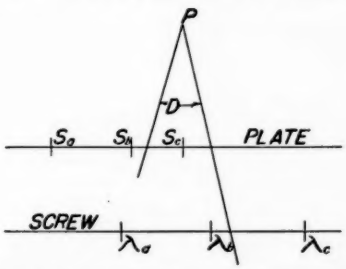

FIG. 2. Schematic diagram of comparator.

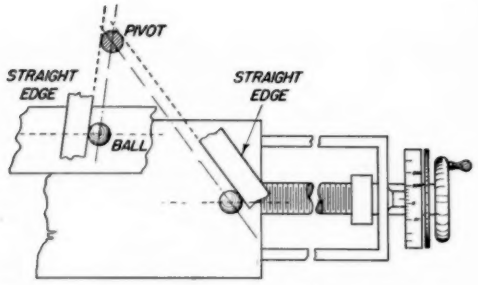

FIG. 3. Mechanical method of realizing the projection.

cision in 1917[8] and found satisfactory. In 1929[9] a crude attachment to a Société Génevoise comparator was built and the success it met with led to the design and construction of the present instrument, a photograph of which is shown in Fig. 4.

It consists essentially of a lower driving carriage sliding on accurately scraped ways and driven by a precision screw of 1 mm pitch. A graduated dial is provided for reading parts of a revolution, and a millimeter scale permits reading of whole turns of the screw. To facilitate putting the instrument into adjustment the zero of this dial and the position of the scale may be varied at will.

Above the driving carriage is a lighter or plate carriage, rolling on steel balls in geometric ways, a pair of *V*'s and a *V* and a flat. Functioning between the two carriages is the transfer mechanism which embodies the principle already shown in Fig. 3. The two straight edges are mounted upon coaxial conical sleeves accurately fitted together and arranged so that they may be set at any angle by a graduated circle with a clamp and tangent screws. The inner sleeve turns on a tapered pivot which is attached to the base of the instrument at a point corresponding to *P* in Fig. 2.

A hardened steel ball affixed to a threaded post may be mounted in any one of a number of threaded holes in the lower carriage while a second similar ball is mounted on the upper or plate carriage. One of the straight edges, in a higher horizontal plane, presses against the latter ball while the other edge, in a lower parallel, plane is moved by the former in such a manner that the normal movement of the lower carriage drives the upper carriage. Contacts are maintained by the usual pulley and weight arrangement. The upper carriage is provided with a slow motion parallel to its slide way to aid in adjustment.

The microscope and the slide way for the upper or plate carriage are both mounted upon a stage traveling at right angles to the main slide and provided with a 1 mm pitch screw with divided head and scale so that the position of the slide way with respect to the pivot may be determined and reproduced at any time.

The particular design shown in Fig. 4 can accommodate a plate or section of a plate 150 mm in length. The working travel of the driving carriage is 204 mm. The dial for the precision screw has 500 divisions. The distances from the pivot to the lines of travel of the holes in the driving carriage range from 9 to 18 cm, while the corresponding distances for the transverse adjustment vary from 7 to 15 cm.

ADJUSTMENT

The comparator is in adjustment when its readings for the three selected standard fiducial lines are in satisfactory agreement with their known values. This is true when: (1) the ball on the driving carriage has been mounted in its proper threaded hole, (2) the transversely traveling stage, and (3) the graduated circle have each been set correctly. An adjustment once made for a given region of the spectrum on a plate taken with a given spectrograph is easily repeated (in about ten minutes) on account of the reproducibility of the settings on the circle and the stage. All that is needed is to keep a record of the data for operations (1), (2) and (3).

This would apply to all the cases in any one laboratory except a few at the start and then the data may be obtained by a graphical method which gives exact results for (1) and results for (2) and (3) which are close enough to permit final adjustments to be carried out readily on the comparator itself.

The full details of these operations would interest only the user of such an instrument and, therefore, they are omitted here. Suffice it to say that the graphical method makes use chiefly of two

[8] L. G. Hoxton, Phys. Rev. **10**, 90 (1917).
[9] L. G. Hoxton, J. Opt. Soc. Am. and Rev. Sci. Inst. **18**, 443 (1929).

pieces of meter stick with three threads attached, while, in the final adjustment, a simple operation brings two of the three standard lines to their proper readings, leaving a deviation for the third line. Since this deviation is small enough to vary linearly with settings (2) and (3), an interpolation process will determine their correct values.

Conclusions

It would be of interest to indicate the degree of flexibility of the comparator, i.e., its applicability to plates from various spectrographs. First there is the limitation of length in the plate accommodated. In this particular model the length of useful travel is 150 mm and, in most cases of prismatic spectra, 130 mm. Plates longer than this would have to be measured in sections. In the opposite direction there are lower limits to the sizes of prismatic spectrographs as will appear later.

In regard to precision, no approximations have been introduced into the geometrical theory. It is to be expected, therefore, that the comparator will yield results on a par with the Hartmann formula unless mechanical difficulties arise. The spectral range covered by a given application of the formula is limited by the tolerance assigned to its deviations for lines other than the three fiducial lines selected. The longer the range the larger the deviations.

A convenient index to assume, for purposes of discussion, is the ratio of the greater dispersion at one end of the range to the lesser value at the other. It is, in fact, a double ratio, which indicates a certain degree of "distortion" from a linear relationship. Thus for a normal spectrum it would have its smallest value, unity, if derived from wave-lengths. It would be greater than unity for the same spectrum if derived from wave numbers. For prismatic spectra it is, for all cases tried, greater for the wave-length than for the corresponding wave number case. The deviations, in general, become greater as this ratio increases. Closely associated with the ratio is the angle D (Fig. 2), the angle set up on the divided circle of the comparator. In the main, the greater the "distortion ratio" the greater the "distortion angle," although it is modified to some extent by the presence of another variable, namely distance of the pivot axis from the travel line of the upper ball.

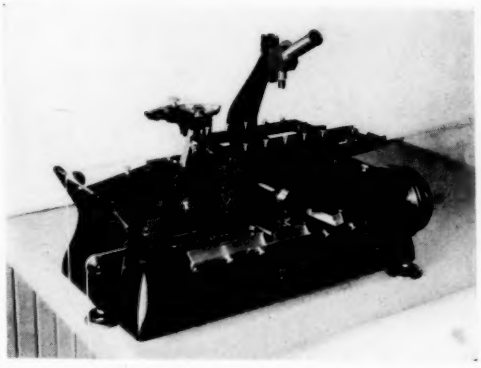

Fig. 4. Photograph of the comparator.

Table I, an example of an application to a prismatic spectrum, serves to illustrate these points. It is self-explanatory except for the letters a, b and c, which mark the fiducial lines. It will be noticed that the deviations in significant figures, the distortion ratio, and the distortion angle are larger for the wave-length, than for the wave number adjustment. Incidentally, while the plate must be measured in two sections, owing to its size, indications are that the Hartmann formula might well be applied in sections also.

The spectrograph just considered is rather large. When the smaller sizes of prismatic spectrographs are tried, limitations begin to appear as already noted. Two instances will be given. One was that of a small Gaertner L 250 quartz spectrograph, where a spectral range from λ2195 to λ3610 occupied 40 mm of the plate. The wave-length distortion ratio was 4.1 while the wave number distortion ratio was 1.6. The second, a Hilger constant deviation instrument, gave a range from λ4045 to λ6495 upon 67 mm of the plate. The two ratios taken in the same order were 6.5 and 2.7, respectively. In both of these cases there was no trouble in setting up and reading wave numbers. (The distortion angles were 31° and 34°, respectively.) An adjustment to wave-length readings, however, would require a closer approach of the plate to the pivot than is permitted by the comparator as it stands. Very minor changes in the instrument would remove this limitation if such should be desired.

TABLE I. *Example of comparator results. B. and L. Littrow prismatic spectrograph. Glass optics. 100 mm section of a 220 mm plate. Iron arc.*

Wave-lengths 10A per mm on screw Circle, 29°0′ Standard	Deviation		Wave Numbers 50 per mm on screw Circle, 10°13′ Standard	Deviation
4903.32	0.00	*a*	20394.4	0.0
4966.10	+ .18		20136.5	−0.8
5049.83	+ .27		19802.6	−1.2
5133.68	+ .32		19479.2	−1.8
5283.63	+ .31		18926.4	−1.4
5446.92	+ .11		18359.0	−0.5
5586.77	+ .01	*b*	17899.4	−0.2
5658.84	− .04		17671.5	+0.1
5914.16	− .44	*	16908.6	+0.8
6191.57	− .07		16151.0	−0.1
6230.73	− .03	*c*	16049.5	−0.1
Distortion ratio	=2.1		*Distortion ratio*	=1.3

* *Excessively faint on the plate.*

These cases, of the small spectrographs, represent the maximum mechanical demands on the comparator. Particularly the angle between the upper straight edge and the line of travel of its contacting ball should not be too acute (Fig. 3). Troubles from this source did not arise.

As we pass from the smaller to the larger prismatic spectrographs all conditions grow more favorable, including the number of decimal places to be read off, while, with a grating spectrum, size is immaterial. The simplest case, in fact, is that of a normal spectrum, the distortion angle being zero. The saving effected here over the conventional comparator is the freedom from the use of a converting factor. Where the grating spectrum is not normal, the comparator will do, wherever 3-point interpolation formula will suffice, provided, of course, that the variation of the dispersion is monotonic over the plate. A stationary value of the dispersion in wave-lengths could be circumvented by resort to wave numbers instead.

If one is working in the neighborhood of a standard line where the Hartmann deviations are near a maximum, it is possible to reduce these to zero or to small values by means of the longitudinal slow motion adjustment on the plate carriage and thus avoid the usual graphical interpolation for these residuals.

Attention is directed to the possibility of incorporating the essentials of this instrument into an attachment to the conventional type comparator. This was done in the preliminary work already mentioned.

The passage of the projection lines (Fig. 3) through the axis of the pivot is not critical. In fact it was found possible[10] in the preliminary work, by varying the "eccentricity" of one of these lines, to reduce and even reverse the signs of the deviations of the Hartmann formula. To incorporate an extra adjustment of this sort, permitting the choice of four fiducial lines, would lead to a less compact design, so that this feature was left out.

A test, in which the room temperature changed by 13°C was made. As was to be expected, a lateral shift in the position of the stage served to correct for this, since we have a case of change in magnification only, the angle D remaining unaffected.

Finally, a matter of minor interest might be pointed out, namely, the possibility of applying the comparator to reading off lengths in terms of an arbitrary unit.

ACKNOWLEDGMENTS

It is a pleasure to make grateful acknowledgments to various persons for aid given during the course of this development: to Professors C. M. Sparrow and F. L. Brown, the former for suggestions concerning some of the principles involved, the latter for help with spectra, for directing tests, and for computations throughout the work; to Mr. A. J. Weed, instrument maker, for constructing the preliminary model; to Dr. E. C. Stevenson, now on the staff of the Jefferson Physical Laboratory, for carrying out extended tests upon it; to Mr. A. W. Kenney of the Experimental Station of the E. I. du Pont de Nemours and Company for the loan of the plate used for Table I; and to Mr. K. W. Harper, who assisted in designing the instrument.

[10] L. G. Hoxton and D. W. Mann, J. Opt. Soc. Am. **25**, 201 (1936).

Analysis of the Spectrum of Hydrogen

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HITHERTO those lines of the spectrum of hydrogen which are most persistent upon prolonged excitation, known collectively as the primary spectrum, have been classified numerically as differences between pairs of levels, in wave numbers, all the levels being members of one series, while the lines of the less persistent parts of the spectrum have been ascribed to differences between other levels, none of which coincide with the primary levels. It may now be shown that the wave numbers of the band lines are accounted for numerically, with a very high degree of precision, as due not to the simple differences between a very large number of independent levels, but to the compounding of simple differences between a comparatively small number of levels, among which the primary levels are included; also that definite series relationships exist between all of the levels, binding them into a single mathematical system.

INTRODUCTORY AND HISTORICAL

Hydrogen at reduced pressure, confined in a suitable container and subjected to the passage of an electric current of sufficient density, at very low voltage emits only a continuous spectrum. If the voltage be gradually increased, at about 16.4 volts changes take place, as a result of which, while the continuous spectrum persists, it alters in character, and very many lines make their appearance. If the current be ample, as the excitation is prolonged, groups of these lines change their relative intensities and gradually disappear, finally leaving only one group, known as the primary spectrum. The lines that fade away are known collectively as the secondary spectrum. When present they accompany the primary lines, both in the far ultraviolet and in the visible and infrared regions, never appearing without at least the first three or four lines of the Balmer series. There are in the visible region about five hundred times as many secondary lines as primary lines, but the first two Balmer lines always are the most intense lines in that region.

When the primary lines appear alone, their orderly arrangement is so conspicuous that it cannot escape observation. In 1885 Balmer found a mathematical formula by which the wave-lengths of these lines were related to one another. Since these lines persist when the temperature is very high and the excitation intense and prolonged, and since free atoms are known to be present in the gas under the conditions of excitation, it is but natural to conclude that the presence of free atoms is a necessary condition for the emission of the primary spectrum. However, free atoms are always present when the secondary spectrum is produced. Experiment does not give us a direct answer as to the origin of either the primary or the secondary systems.

In the absence of conclusive evidence, the assumption that the primary lines originated in free atoms and the secondary lines in molecules or ions, preferably the molecule H_2, was generally tacitly accepted. In 1913 Bohr, on the basis of this assumption, proposed his theory of structure of the hydrogen atom, which accounted numerically for the lines, but not for the continuous spectrum that always accompanies them.

There followed various attempts to produce a theoretical model of the molecule H_2 in keeping with the assumptions adopted by Bohr to account for the lines of the primary spectrum. There also followed attempts to classify the secondary lines, independently, on the basis of observable mathematical relationships of wave numbers. The writer became interested in this work of classification in 1924, very little progress having been made in it before then, and has continued his work until the present time. In 1922 Merton and Barratt had published an admirable list of wavelengths and wave numbers of about 1300 secondary lines, with a review of all previous work on the secondary spectrum, and Professor O. W. Richardson and his associates were diligently attempting to discover regularities and to establish the basis for systematic classification.

Professor Richardson's work, published by the

Royal Society in numerous papers as it progressed, was finally collected and republished in book form in 1934. That work is essential to anyone who attempts to understand the secondary spectrum of hydrogen, and it contains adequate references to all important work published at an earlier date. Meanwhile essential work in the Schumann region was done by Dieke and Hopfield and others, while the very accurate measurements of Gale, Monk and Lee became available in 1927. The present writer has no facilities for experimental work, but has availed himself of measurements provided by others, including many besides those mentioned; and he also has had the aid of all of the classification papers of others, as they have been published.

All mathematical schemes for classifying many lined or band spectra, whatever theories may have been entertained by those who did the classification work, have actually proceeded by seeking constant, or regularly progressing differences between wave numbers. The first attempts were at arranging lines into "bands," by means of regularities in "second differences." Later, these bands were classified into systems by means of other regularly recurring difference numbers, and a great many previous classifications of a tentative nature rejected because they did not fit into any comprehensive scheme.

Professor Richardson discovered two systems of "horizontal" difference numbers which recur very many times in different sub-systems, and became the means for determining the classification of a very large number of lines with great confidence. The writer accepts all of Professor Richardson's classifications which are thus confirmed; but he accounts for these difference numbers in a manner not hitherto employed. The general scheme is as follows:

Instead of postulating a very large number of different levels for the secondary spectrum, between pairs of which individual lines are differences, I have entertained the hypothesis that the number of levels is comparatively small, and that the lines are due to compounding of differences between pairs of levels. In band structure the first line of each series is a compound of the null with another difference which is a simple difference between levels. Successive lines of each series are compounded from the first line, by one or more simple differences. It has been found possible to account for all of the known bands in this manner, and to ascertain the levels. From these known levels it has been possible to predict the principal nulls of band systems hitherto unknown, and by means of known differences to determine the nature of band structures which differ from those by the discovery of which the beginnings of analysis of this spectrum were made possible.

The Table of Levels

As the quantum theory of band structure is not employed in this analysis, the principal levels and the most important differences which recur many times in various combinations in the structure of the various band systems are given in wave numbers in Fig. 1. For indexing purposes each level is designated by some combination of the letters *a* and *b* in the left-hand column. Those in which only the letter *a* is used are the primary levels. The wave numbers are given in the third column. All other numbers occurring in the table are differences between pairs of levels, which occur in band structure, compounded according to very interesting schemes which space accorded to this presentation does not suffice to set forth.

In the second column the differences 311.57 to 181.98 occur between the nulls of bands in Professor Richardson's alpha and beta systems, and in a number of other systems classified by myself. The numbers 353.0 to 303.4 occur as similar differences in his gamma bands, and in one of his infrared systems, extended by myself by horizontal extrapolation in a manner to give the 0.0 band. The numbers 54.15 to 51.43 occur as differences between nulls and *RO* lines in various places. 1907.46 found in the fourth column is the most important difference number in the far ultraviolet system of Hopfield, measured in absorption. Other numbers in the fourth column combine with the number 1318.34 to produce "horizontal" differences between nulls in numerous band groups classified by Richardson, while such numbers as 136.50 to 134.32 combine with the number 2524.34 to produce horizontal null differences in numerous other groups which Richardson discovered, including the alpha and the beta bands, which are the most regular of all.

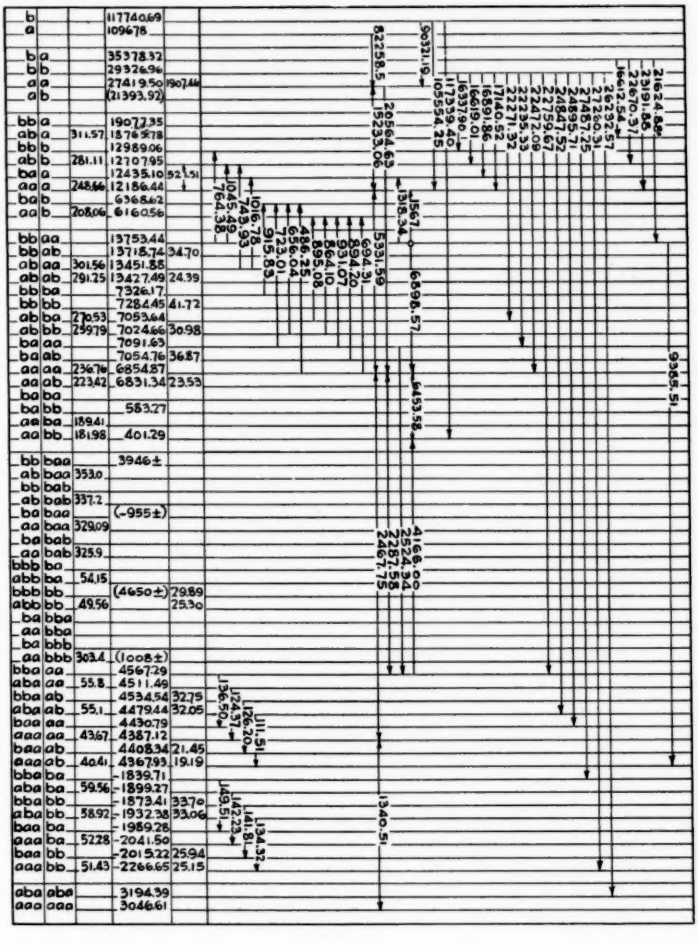

FIG. 1.

The number 521.51 in the fourth column and all of the numbers such as 764.38 which are differences between levels as indicated by vertical lines to the right of the fourth column occur as differences between band nulls in various band systems. There are several band systems which originate in nulls that are simple differences between levels. These are given in the right-hand half of the table, the levels concerned being joined by vertical lines. Of these, three extensive systems are in the Schumann region, the wave number of highest frequency concerned being 117740.69 for each of them. In the visible and near ultraviolet region thirteen nulls originate in combinations in which 29326.96 is the largest wave number, and four in combinations in which 35378.32 is the largest wave number. There are several systems in the infrared, but only one of them has been traced fully, because their principal nulls are not within the region for which sufficiently complete measurements have been made. For this one infrared system I have obtained the origin and principal series by extrapolation of "horizontal" differences. The level of highest frequency is 13753.44, a number which enters into at least seven different combinations to produce differences which are important in the structure of the secondary spectrum.

Combinations Involving Primary Levels

One vertical line in the table gives those primary combinations which give rise to the first lines of the Lyman, Balmer, Paschen and Brackett series. A line is also devoted to the second Balmer line, which enters into combination with another difference to produce the *B3–A7* null of Dieke and Hopfield. The combinations involving primary levels which are most important in the secondary spectrum as thus far classified, including all of the strong lines, are as follows:

With *aa* = 27419.50	*b–aa*	90321.19
	bb–aa	1907.46
With *aaa* = 12186.44	*b–aaa*	105554.25
	bb–aaa	17140.52
	bbaa–aaa	1567.00
	baa–aaa	248.66
With *aaaa* = 6854.87	*bb–aaaa*	22472.09
	aa–aaaa	20564.63
	bbaa–aaaa	6898.57
	aaaa–aabb	6453.58
	aaaa–bbaaa	2287.58
	baaa–aaaa	236.76
	aaaa–aaab	23.53

Series Relationships

From the table we may select a number of groups of levels representing mathematical series. Among these are:

a, aa, aaa, aaaa, etc., represented by the formula $N \div n^2$ in which n is an integer and N the Rydberg number. These levels combine in pairs to produce the lines of the primary spectrum.

b, bb, bbb, bbbb, etc., which may be represented by the formula $N \div (nb)^2$ in which b is a fraction, somewhat variable, between the values 0.96515 and 0.97+. No combinations of these levels with one another occur; but they combine with other levels in various band structures.

bb, abb, abba, etc., represented by the formula $N \div (2+(n+2b)^2)$. Combinations of these give rise to the principal nulls of the alpha and beta systems, so fully worked out by Richardson.

aa, baa, baab, etc., comprise a series represented by the formula $N \div (2+nb)^2$. These levels do not combine with one another to produce nulls, but enter into other combinations.

ba, aba, abab, aabab, aababa, etc., comprise a series which, if the terms combined with one another, would give rise to "displaced" series, very similar to those which Paschen found in neon.

Every level can be represented by a modified Rydberg formula, or a combination of such formulae, and there are as many possible levels as there are combinations of the letters *a* and *b*, as indicated in the table.

Thirty-three tables dealing with band structure have been prepared showing how these difference numbers and others combine to account for the nulls and the leading lines of all of the band systems that are now known, which include all of the strong lines and a very large number of those of very small intensity—about two thousand in all. It will be observed by those familiar with this kind of work that these numerical relationships are very precise, and as the same difference numbers occur many times in entirely different combinations, there can be very little doubt about the correctness of the classifications, whatever interpretation may be placed upon them. It is impossible in the space now available in this journal to give these tables, but by writing to the author copies of them may be obtained by persons who wish to examine them carefully. These tables include the analysis of five band systems for which no data have been published hitherto, as well as extensions and interrelations of band systems of all sub-systems now recognized. In no previous publication have the nulls been obtained with the same precision, the method involving no arithmetical processes more complicated than subtraction.

Glass Color Filters for Special Applications

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The spectrophotometric data for one thickness of a glass is sufficient for calculating these data for any other thickness by a method here described, using either an ordinary slide rule or a special table. Calculation is made of the thickness required of two special glasses used in combination, one yellow, the other a new type of blue green, for correcting the spectral response of a photronic cell to the spectral luminosity response of the eye.

IN the production of color filters to meet special requirements, two separate techniques are required; first the technique involved in the glass makers art, and second the optical and mathematical techniques of spectrophotometric analysis and calculation necessary to obtain and combine the data for two or more coloring materials so as to determine how close an approximation to the desired result may be secured by the use of manufacturable glasses. In this paper the main emphasis is placed on mathematical technique. The conclusions must, however, be guided by consideration of the known variations in color from melt to melt and the limited precision of spectrophotometric measurements.

Transmission Calculation of a Given Thickness of Glass When the Spectral Transmission of Another Thickness is Known

Direct calculation of the transmission of one thickness of glass when that for another thickness is known can be made only for homogeneous light except in the case of spectrally nonselective (gray) glass. The same restriction applies self-evidently to varying concentrations of colored solutions. Suppose one thickness of glass transmits one-half the incident light of one wavelength. Two thicknesses will transmit one-half of one-half, or one-quarter; a third glass will transmit one-half of this again or one-eighth and so on, leading to the formula $T_n = T^n$ where T_n is the transmission of n pieces of glass, T being the transmission of each piece. Using logarithms the formula becomes $\log T_n = n \log T$ ($\log_{10} T$ for a single piece is called density, D). This formula neglects the fact that the later pieces of glass reflect part of the light backwards toward the source and the earlier ones reflect some of this light in the original direction so that part of the reflected light is not lost after all.

Consider a single homogeneous piece of colored glass of variable thickness t. The surface loss due mostly to reflection but partly to other causes is constant and assumed to be nonselective. The property which varies with thickness is then not primarily transmission (ratio of light leaving the second surface to that incident upon the first surface) but transmittance (ratio of light incident upon the second surface to that leaving the first surface) or in other words, transmission corrected for surface losses.

In general this nonselective surface reflection loss is about 4 percent for each surface or 8 percent for the two surfaces. While the reflectance varies with the refractive index of the glass, its surface condition, and the angle of incidence, and while there is a small effect of multiple reflection, the transmission of thin, colorless polished glass has been measured usually as 92 percent, although in a few cases as high as 94 percent and by special treatment it may go higher.[1, 2] The multiple reflection of a single piece amounts to about 4 percent reflected back by the second surface, of which 4 percent or 0.16 percent of the whole is again reflected forward by the first surface. This amount is too small to be significant and is beyond the accuracy of any spectrophotometric measurements made in prac-

[1] F. Kollmorgen, "Light Transmission Through Telescopes," Trans. I. E. S. 11, 220 (1916).
[2] *The Manufacture of Optical Glass and of Optical Systems*, (A War Time Problem) Gov't. Printing Office 1921; Ordinance Department Document 2037. Treatment of polished glass surfaces to reduce the amount of light reflected, p. 76.

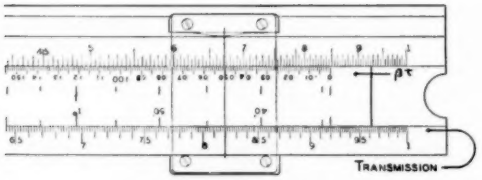

FIG. 1. Slide rule with slide reversed and inverted. The slide is set so that the zero of the log scale is opposite 0.92 on the lower scale. The log scale then gives the βt value corresponding to transmission on the lower or number scale, thus transmission 0.92 corresponds to $\beta t = 0$; transmission 0.82, $\beta t = -0.05$; transmission 0.65, $\beta t = -0.15$; etc. Some slide rules which are arranged differently may require a little study to find the log and number scales which will give the same results.

tical calculation of color filters. The correction ordinarily applied is therefore to assume that transmission is 92 percent of transmittance.

Assign the symbols:

T = transmission of the piece of glass
C = transmittance per mm glass
C_t = transmittance for t mm glass
t = thickness
$\beta = \log_{10}$ transmittance for 1 mm thickness.

Then from the above $T = 0.92C_t$, $C_t = T/0.92$. By reasoning similar to that for the separate pieces of glass previously described

$$C_t = C^t$$

$$\log_{10} \text{transmittance} = \log_{10} C_t = \beta t$$

from which is derived $\beta t = \log_{10}(T/0.92) = \log_{10} T - 0.0362$.

As transmission and transmittance are always less than unity, the logarithms are always negative. I find it simpler to use these logarithms in the pure negative form than to use them in the usual mixed form; i.e., I use for $\log_{10} 0.5$ (i.e., $\log_{10} \frac{1}{2}$) not the mixed form $-1+0.699$ or $9.699-10$ but the value -0.301. When the spectrophotometric data are plotted in the logarithmic form the zero line (100 percent transmittance) is at the top and the rest of the curve is below this. By so doing the spectrophotometric curves and βt curves go up or down together and do not cross.

Spectrophotometric data may be determined directly as transmittance by measuring the transmission of the glass compared to a thin clear glass of approximately the same refractive index and surface finish or by immersion in a equal index liquid to remove surface reflection. The universal practice, however, is to express such data as transmissions. If transmittance data were available the calculations could be made on a special log-log slide rule constructed for the purpose by Keuffel and Esser. As a correction is necessary the logarithmic calculation is the simplest and can be made with any slide rule (Fig. 1) or by the help of a special table. (Table I).

CALCULATION PROCEDURE

In Corning we have found the most expeditious way of converting one transmission curve to another is to use data sheets ruled in columns. In column (1) are wave-lengths; (2) the corresponding transmissions as measured; (3) the values of βt as read from the inverted slide rule or the special table for the given thickness; (4) the new value of βt for the desired thickness proportional to the relative values of t calculated on a slide rule (it is not necessary to calculate β for thickness of 1 mm although this may be done if desired); (5) transmission of new thickness as read from the table or inverted slide rule.

VARIATION OF LIGHT TRANSMISSION WITH CONCENTRATION OF COLORING MATERIAL

The transmission of a glass depends not only upon the kind and concentration of coloring material used but also upon the state of oxidation or reduction of the melt and the composition of the glass in which the coloring agent is dissolved. According to the simple theory (Beer's law) if the concentration of the coloring material is doubled and the thickness of the glass is reduced to one-half resulting in the same amount of coloring material per square centimeter, one would expect the resulting color to be the same. This holds approximately in dilute solutions but with concentrated solutions the coloring agent becomes itself a significant part of the solvent and reacting upon itself alters the color.

The coloring material is mixed with the other materials of the glass making "batch" shoveled into a crucible holding from 100 lb. to 3,000 lb. of glass and held at a temperature of 1200° to 1300°C for 24 to 72 hours to melt thoroughly, mix and allow bubbles to float out (fining process). At this temperature all but the most refractory substances volatilize to a greater or less extent so that the composition of the glass differs somewhat from that calculated from the

batch. This precludes accurate prediction of the exact color which will be obtained. However, a close approximation to a given desired color can be secured by taking into consideration the glassmakers knowledge accumulated from long years of experience. When a melt is ready to work the first few samples made are tested on a photometer to determine color density and whether it is "off color" due to the greater volatilization of some of the coloring materials, caused by variations in the length and temperature of run. Simple density differences can be corrected by control of thickness of pressing or blowing, or with color filters the necessary finished thickness can be determined for each melt. It is, however, necessary to decide as to whether or not to work the melt and what thickness it must be pressed within a few minutes after the melt is in condition to work. A few colors are changed during the annealing process for which the necessary allowance must be made, as, for example, Corning Daylite glass becomes lighter and less pink after annealing. The selenium reds and yellows of the sharp spectrum cut-off type are also subject to great color change caused by heat treatment. For polished color filters of

TABLE I.

	TRANSMISSION											TRANSMISSION									
βt	9	8	7	6	5	4	3	2	1	0	βt	9	8	7	6	5	4	3	2	1	0
99	9226	9247	9268	9290	**9311**	9333	9354	9376	9397	**9419**	49	2917	2924	2931	2938	2944	2951	2958	2965	2972	2979
98	9441	9462	9484	**9506**	9528	9550	9572	9594	**9616**	9638	48	2985	2992	2999	**3006**	3013	3020	3027	3034	3041	3048
97	9661	9683	**9705**	9727	9750	9772	9795	**9817**	9840	9863	47	3055	3062	3069	3076	3083	3090	3097	**3105**	3112	3119
96	9886	**9908**	9931	9954	9977	**1000**	1002	1005	1007	1009	46	3126	3133	3141	3148	3155	3162	3170	3177	3184	3192
95	1012	1014	1016	1019	1021	1023	1026	1028	1030	1033	45	3199	**3206**	3214	3221	3228	3236	3243	3251	3258	3266
94	1035	1038	1040	1042	1045	1047	1050	1052	1054	1057	44	3273	3281	3289	3296	**3304**	3311	3319	3327	3334	3342
93	1059	1062	1064	1067	1069	1072	1074	1076	1079	1081	43	3350	3357	3365	3373	3381	3388	3396	**3404**	3412	3420
92	1084	1086	1089	1091	1094	1096	1099	**1102**	1104	1107	42	3428	3436	3443	3451	3459	3467	3475	3483	3491	3499
91	1109	1112	1114	1117	1119	1122	1125	1127	1130	1132	41	**3508**	3516	3524	3532	3540	3548	3556	3565	3573	3581
90	1135	1138	1140	1143	1146	1148	1151	1153	1156	1159	40	3589	3597	**3606**	3614	3622	3631	3639	3648	3656	3664
89	1161	1164	1167	1169	1172	1175	1178	1180	1183	1186	39	3673	3681	3690	3698	**3707**	3715	3724	3733	3741	3750
88	1189	1191	1194	1197	1199	**1202**	1205	1208	1211	1213	38	3758	3767	3776	3784	3793	**3802**	3811	3819	3828	3837
87	1216	1219	1222	1225	1227	1230	1233	1236	1239	1242	37	3846	3855	3864	3873	3882	3890	3899	**3908**	3917	3926
86	1245	1247	1250	1253	1256	1259	1262	1265	1268	1271	36	3936	3945	3954	3963	3972	3981	3990	3999	**4009**	4018
85	1274	1276	1279	1282	1285	1288	1291	1294	1297	**1300**	35	4027	4036	4046	4055	4064	4074	4083	4093	**4102**	4111
84	1303	1306	1309	1312	1315	1318	1321	1324	1327	1330	34	4121	4130	4140	4150	4159	4169	4178	4188	4198	**4207**
83	1334	1337	1340	1343	1346	1349	1352	1355	1358	1361	33	4217	4227	4236	4246	4256	4266	4276	4285	4295	**4305**
82	1365	1368	1371	1374	1377	1380	1384	1387	1390	1393	32	4315	4325	4335	4345	4355	4365	4375	4385	4395	**4406**
81	1396	**1400**	1403	1406	1409	1413	1416	1419	1422	1426	31	4416	4426	4436	4446	4457	4467	4477	4487	4498	**4508**
80	1429	1432	1435	1439	1442	1445	1449	1452	1455	1459	30	4519	4529	4539	4550	4560	4571	4581	4592	**4603**	4613
79	1462	1466	1469	1472	1476	1479	1483	1486	1489	1493	29	4624	4634	4645	4656	4667	4677	4688	4699	**4710**	4721
78	1496	**1500**	1503	1507	1510	1514	1517	1521	1524	1528	28	4732	4742	4753	4764	4775	4786	4797	**4808**	4819	4831
77	1531	1535	1538	1542	1545	1549	1552	1556	1560	1563	27	4842	4853	4864	4875	4887	4898	**4909**	4920	4932	4943
76	1567	1570	1574	1578	1581	1585	1589	1592	1596	**1600**	26	4955	4966	4977	4989	**5000**	5012	5023	5035	5047	5058
75	1603	1607	1611	1614	1618	1622	1626	1629	1633	1637	25	5070	5082	5093	**5105**	5117	5129	5140	5152	5164	5176
74	1641	1644	1648	1652	1656	1660	1663	1667	1671	1675	24	5188	**5200**	5212	5224	5236	5248	5260	5272	5284	5297
73	1679	1683	1687	1690	1694	1698	**1702**	1706	1710	1714	23	**5309**	5321	5333	5346	5358	5370	5383	5395	**5408**	5420
72	1718	1722	1726	1730	1734	1738	1742	1746	1750	1754	22	5433	5445	5458	5470	5483	5495	**5508**	5521	5534	5546
71	1758	1762	1766	1770	1774	1778	1782	1786	1791	1795	21	5559	5572	5585	5598	**5610**	5623	5636	5649	5662	5675
70	1799	**1803**	1807	1811	1816	1820	1824	1828	1832	1837	20	5689	**5702**	5715	5728	5741	5754	5768	5781	5794	**5808**
69	1841	1845	1849	1854	1858	1862	1866	1871	1875	1879	19	5821	5834	5848	5861	5875	5888	**5902**	5916	5929	5943
68	1884	1888	1892	1897	**1901**	1905	1910	1914	1919	1923	18	5957	5970	5984	5998	**6012**	6026	6039	6053	6067	6081
67	1928	1932	1936	1941	1945	1950	1954	1959	1963	1968	17	6095	**6109**	6124	6138	6152	6166	6180	6194	**6209**	6223
66	1972	1977	1982	1986	1991	1995	**2000**	2004	2009	2014	16	6237	6252	6266	6281	6295	**6310**	6324	6339	6353	6368
65	2018	2023	2028	2032	2037	2042	2046	2051	2056	2061	15	6383	6397	**6412**	6427	6442	6457	6471	6486	**6501**	6516
64	2065	2070	2075	2080	2084	2089	2094	2099	**2104**	2109	14	6531	6546	6561	6577	6592	**6607**	6622	6637	6653	6668
63	2113	2118	2123	2128	2133	2138	2143	2148	2153	2158	13	6683	6699	**6714**	6730	6745	6761	6776	6792	**6808**	6823
62	2163	2168	2173	2178	2183	2188	2193	2198	**2203**	2208	12	6839	6855	6871	6887	**6902**	6918	6934	6950	6966	6982
61	2213	2218	2223	2228	2234	2239	2244	2249	2254	2259	11	6998	**7015**	7031	7047	7063	7079	7096	**7112**	7129	7145
60	2265	2270	2275	2280	2286	2291	2296	**2301**	2307	2312	10	7161	7178	7194	**7211**	7228	7244	7261	7278	7295	**7311**
59	2317	2323	2328	2333	2339	2344	2350	2355	2360	2366	09	7328	7345	7362	7379	7396	**7413**	7430	7447	7464	7482
58	2371	2377	2382	2388	2393	2399	**2404**	2410	2415	2421	08	7499	**7516**	7534	7551	7568	7586	**7603**	7621	7638	7656
57	2427	2432	2438	2443	2449	2455	2460	2466	2472	2477	07	7674	7691	**7709**	7727	7745	7762	7780	7798	**7816**	7834
56	2483	2489	2495	**2500**	2506	2512	2518	2523	2529	2535	06	7852	7870	7889	**7907**	7925	7943	7962	7980	7998	**8017**
55	2541	2547	2553	2559	2564	2570	2576	2582	2588	2594	05	8035	8054	8072	8091	**8110**	8128	8147	8166	8185	**8204**
54	**2600**	2606	2612	2618	2624	2630	2636	2642	2649	2655	04	8222	8241	8260	8279	8299	**8318**	8337	8356	8375	8395
53	2661	2667	2673	2679	2685	2692	2698	**2704**	2710	2716	03	**8414**	8433	8453	8472	8492	**8511**	8531	8551	8570	8590
52	2723	2729	2735	2742	2748	2754	2761	2767	2773	2780	02	**8610**	8630	8650	8670	8690	**8710**	8730	8750	8770	8790
51	2786	2793	2799	**2805**	2812	2818	2825	2831	2838	2844	01	**8810**	8831	8851	8872	8892	**8913**	8933	8954	8974	8995
50	2851	2858	2864	2871	2877	2884	2891	2897	**2904**	2911	00	**9016**	9036	9057	9078	9099	**9120**	9141	9162	9183	**9204**
	9	8	7	6	5	4	3	2	1	0		9	8	7	6	5	4	3	2	1	0

Rearranged by H. P. Gage

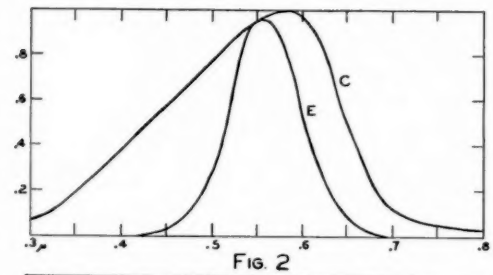

FIG. 2

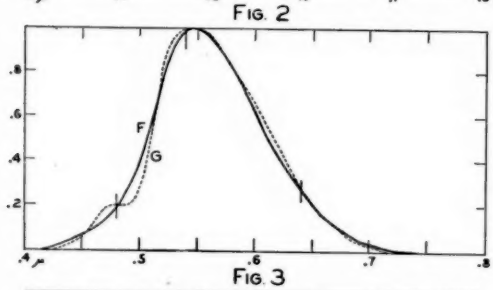

FIG. 3

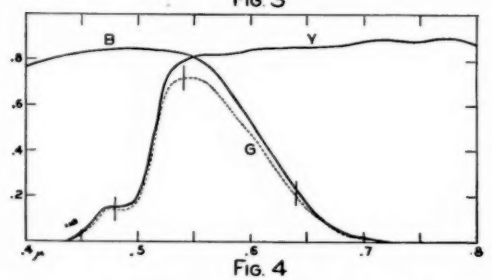

FIG. 4

FIG. 2. *C*, spectral sensitivity of cell; *E*, spectral sensitivity of eye. FIG. 3. *F*, transmittance of theoretical correction filter for cell; *G*, transmittance of glass filter calculated to intersect curve *F* at the three points; 0.48μ, 0.54μ, 0.64μ. FIG. 4. *B*, transmission of blue-green element; *Y*, transmission of yellow element; *G*, transmission of the two elements cemented together.

this type of glass which must be uniformly colored through the entire thickness not a great deal can be done by altering finished thickness as most of the color depends upon the wave-length of the sharp spectral cut-off which is only slightly affected by thickness.

GLASS CORRECTING FILTERS

In the theoretical adjustment of correcting filters it is necessary to know

1. The curves to be corrected,
2. The final result to be obtained,
3. The available coloring materials with their spectral transmission.

THE PHOTRONIC CELL

The Weston photronic cell has a spectral response somewhat as shown in Fig. 2*C* while the eye has a luminous response as shown in curve 2*E*. From this it is calculated that the required transmission of the filter is as shown in curve 3*G*. Earlier correcting filters had been made using a liquid filter formulated by Dr. Brian O'Brien[3] and a dyed gelatin filter prepared by the Eastman Kodak Company. The specific data for the photronic cells used in this calculation were supplied by Dr. M. E. Fogle of the Weston Electrical Instrument Corporation[4, 5] and the calculations used in the filters finally specified were made by him. The filters are composed from two glasses *b* and *y* illustrated in Fig. 4. These were first made in small experimental melts of one pound or less. Glasses obviously unsuitable were rejected; likely candidates were plane polished and spectrophotometered by the Electrical Testing Laboratories under the direct supervision of Dr. Roger S. Estey. A yellow glass was soon selected having the spectral transmission shown in Fig. 4*Y* and a melt of the smallest commercial size was made. The pale blue-green glass (Fig. 4*B*) was more difficult to obtain as the coloring agent dissolved in glasses of known commercial types did not have as sharp a spectral cut-off as was required and in general absorbed too far towards the shorter wave-lengths resulting in a low transmission for the finished filter, the maximum point of which is at 0.546μ. The ideal filter should not absorb anything at this wave-length.

It was found that a special type of glass to which was added the coloring agent did give very nearly the theoretically desirable spectral transmission and this combined with the yellow glass gives the transmission curve, Fig. 3*G*. Inasmuch as the blue-green element did not give the desired result when dissolved in the yellow glass, the yellow element was tried in the special glass. This combination did not work at all as the

[3] B. O'Brien, "Photo-Cell Filter Combination with Spectral Sensitivity Approximating the Visibility Function," J. O. S. A., **22**, 427 (1932).

[4] M. E. Fogle, "New Color Corrected Photronic Cells for Accurate Light Measurements," Trans. I. E. S., **31**, 773 (1936).

[5] M. E. Fogle, "Application of Photronic Photo-Cell to Chemical Processes," Trans. Electrochem. Soc., **69**, 443 (1936).

resulting color had no resemblance to what was desired, another instance of the profound influence of the solvent upon the material dissolved.

Calculation of Relative Thickness of Yellow and Blue Elements

There being two glasses, there are two variables which may be inserted in equations, namely the thicknesses of the finished glasses which we will call b and y which are substituted in the equations wherever thickness t occurs. The values of $\beta = \log_{10}$ transmittance for unit thickness are constant for a given glass but vary with wave-length and should be identified by a subscript indicating the given wave-length. Three points on the desired final curve at suitable wave-lengths are selected and thicknesses of the two glasses are calculated so that the transmissions through them at these wave-lengths shall be in the same ratios as the transmissions through the desired filter. That is to say the transmissions through the actual glass filter at these points shall be equal to the transmissions of the theoretically perfect filter multiplied by a constant factor E.

Calculation of filters to be correct for the three wave-lengths $\lambda = 0.480\mu$, 0.540μ, and 0.640μ; with check on 0.540μ.

In the following calculation the symbols used are:

βt = log transmittance
βt_λ = log transmittance for a given wave-length
$\beta t_{.54}$ = log transmittance for wave-length 0.540μ
$\beta' = \beta t_\lambda - \beta t_{.54}$, is the logarithm of the ratio of the desired transmission at the given wave-length to that at 0.54μ.
βy and βg, subscripts refer to the yellow and blue-green glasses.
$\beta'_\lambda y$, etc. The subscript refers to wave-length, y and b are the thicknesses of the two glasses.

Note that all values of β are negative. Some values of β' are positive and it has been deemed necessary to so indicate in the calculation.

Wave-length, λ	0.480μ	0.540μ	0.580μ	0.640μ
Desired transmittance	.19	.991	.833	.275
Desired log transmittance βt	−.721	−.004	−.079	−.561
Required $\beta' = \beta t_\lambda - \beta t_{.54}$	−.717	.000	−.075	−.557
Measured transmission yellow glass, thickness $y = 2$ mm	.16	.805	.84	.86
βt for yellow glass	−.760	−.058	−.040	−.030
β " " "	−3.80	−.029	−.020	−.015
Measured transmission blue-green glass	.865	.855	.735	.335
β for blue-green thickness $b = 1.20$	−.027	−.032	−.098	−.439
β for blue-green thickness $b = 1$	−.023	−.027	−.082	−.366
$\beta' y (\beta_\lambda - \beta_{.54})$ for yellow glass	−.351	0	+.009	+.014
β'_b for blue-green glass	+.004	0	−.055	−.339

Equation used $\beta'_\lambda y + \beta'_\lambda \quad b$ = required β'_λ

Substitute for two values of λ and solve for the two thicknesses y and b

$\lambda = 0.480\mu$	$-0.351y$	$+0.004b$	$= -0.717$
$\lambda = 0.640\mu \times 0.0118$, add	$+0.000165y$	$-.004b$	$= -0.0066$
	$-0.351y$		$= -0.724$
	y		$= -2.06$ mm
$\lambda = 0.640\mu$	$+0.014y$	$-0.339b$	$= -0.557$
substitute	$y = 2.06 + .029$	$-\ .339b$	$= -\ .557$
		$-.339b$	$= -\ .586$
		b	$= 1.73$ mm

Check

βy, $y = 2.06$ (all values negative)	0.784	0.060	0.041	0.031
βb, $b = 1.73$	.040	.047	.142	.633
$\beta y + \beta b$	.824	.107	.183	.664
− desired βt	.721	.004	.079	.561
dif. = $\log_{10}$ factor E (= .789)	.103	.103	.104	.103

Having made the calculations for the thickness of the two elements, disks of the glasses are polished to the thicknesses specified and tried as a filter with the photronic cell using light sources of known candlepower but of differing spectral composition, such, for example, as tungsten lamps operating at different color temperatures, sodium vapor lamps, neon lamps, mercury vapor lamps and possibly natural daylight. Also, with tungsten lamps operated at known color temperature and a series of color filters such as the standards adopted by railway signal engineers (AAR specification 6935) which have been carefully measured at the National Bureau of Standards. It is not at all certain that the results will be consistent. The particular cell tested may or may not have the same spectral sensitivity as the ones originally used to determine the response curve. The visual response of the observers setting the candlepower of the light source when its color differs considerably from that of the tungsten lamp standards may differ from that of the hypothetical standard I.C.I. observer. It will be remembered that last year there was a paper[6] on the differences in light output of the same mercury vapor lamps as measured by different laboratories. By the use of a series of filter elements of slightly different thickness from those calculated above and with suitable light sources of differing color it is possible to alter the filter-cell combination so that it gives the same relative readings as do the assigned values of illumination of the sources. The filters actually specified by Dr. Fogle as the result of his later experiments with the color sensitivity of the cells, and his further calculations as a matter of fact do differ slightly from the values here presented as an illustration of method.

[6] W. E. Forsythe, "Present Status of Photometry," Trans. I. E. S. **31**, 181 (1936).

Adjustment of Later Melts of Filter Glass

Owing to unavoidable variation in transmission from melt to melt, any given melt must be compared with a standard to determine whether it is "off color" and of the correct density. With the same glass composition and approximately the same concentration when a single coloring agent is used, the general shape of the spectral curve should be the same. A slight shift in the shape of this curve will generally be apparent by direct visual comparison of the sample and standard held side by side. For this reason spectrophotometric test at a single wavelength should enable one to make thickness adjustments to get the desired absorption. (This was the method employed in maintaining the shades of Welders glass.)

The above description of the solution of the problem involving the combination of two colored glasses, each of which can be examined separately and whose thickness may be adjusted separately in order to accurately produce a predetermined result may also serve to indicate possible complications involved when several coloring materials are combined in the same melt of glass and when the variable conditions of volatilization, oxidation reduction, and heat treatment all contribute to the uncertainty of the final result. A satisfactory color can be and is secured in quantity production when certain small but sufficient tolerances are allowed, the limits of which are defined by physical standards, "limit glasses" selected for certain special requirements such as railway, lighthouse, aviation, and traffic signals.

The Constancy of the Blue Arc Phenomenon

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THE blue arc phenomenon[1] is the pair of luminous arcs which appear to the practiced observer as connecting a parafoveal stimulus with the projected blind spot.[2] Since their original description by Purkinje[3] these entoptic arcs have been repeatedly observed but never wholly explained.[4] They have been shown by Snell and Amberson to correspond spatially with the curved courses of the papillo-macular fiber bundles and to be quite certainly a conscious resultant of secondary stimulation from those bundles.[5] But the nature of the secondary stimulus and the receptors for it are still unknown.[6]

This paper reports new data by a new technique[7] bearing upon an extraordinary feature of the blue arc phenomenon. This feature is its relative constancy. Not only do the arcs have their characteristic form but under ordinary conditions of qualitative observation they have usually been reported as of approximately uniform hue.[8] Even under quantitative conditions with wide variation in stimulus intensity, the brilliance of the phenomenon has been found by Troland to remain substantially unchanged.[9] Furthermore, with steady stimulus and fixation, the duration of the arcs approaches constancy.[10]

By investigating the degree and conditions of this relative independence of primary stimulus and secondary response, it was believed that further insight might be gained concerning the functional significance of the response itself. To that end, then, data were taken with controlled variation in the chromaticity, retinal illumination, and duration of the inducing stimulus, and measurements were made of the corresponding attributive characteristics of the entoptic phenomenon.

COLORIMETRIC TECHNIQUE

Preliminary sessions for familiarization with the rather exacting technique confirmed two of the conditions upon which the seeing of the arcs unquestionably depends. One of these conditions is the retinal area upon which the primary stimulus falls. The effective area is found to lie in the macular region on the temporal side of the fovea. A common difficulty of the unpracticed observer is the natural tendency to eye movement toward the apparent position of the arcs which automatically displaces the stimulus. The second condition is the appropriate direction of attention. Even with the stimulus properly placed the new observer frequently fails to see the arcs simply because he does not know just what to expect or where to look. He, as the novice attempting to observe after-images, must analyze

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[1] Variously known as the blue arc effect, the blue arcs of the retina, the blue brushes, le phénomène des arcs, die zwei Bogenstreifen, die Nebelbogen, das Neuroaktionsphosphen, and die Elliptischen Lichtstreifen.

[2] Favorable conditions of occurrence of the phenomenon are given in the section on colorimetric technique.

[3] J. E. Purkinje, Beobachtungen und Versuche zur Physiologie der Sinne, **2**, 74 (1825).

[4] A complete bibliography of the arcs may be found in the following available papers: D. B. Judd, Nat. Bur. Stand. J. Research **2**, 441 (1929) and B. Friedman, Arch. Ophth. **6**, 663 (1931). In the present paper, therefore, it has usually seemed sufficient simply to cite the name of the investigator.

[5] The principal argument is the close spatial relation of arcs and bundles. But there are also the less brilliant blue lancet, spike, or Lanzettstreifen, and the blue halo, oval, haze, glow or retinaktionsphosphen, which are believed to be allied effects involving neighboring areas and which have been discussed by H. Gertz, Ellis, Ladd-Franklin and Amberson.

[6] The theories of the arcs have been summarized by B. Friedman, but only two of them still seem plausible, i.e., the electrical which is favored by H. Gertz, O. Gertz, Troland, Amberson, Davis, Ellis, Snell, Friedman, and the bioluminescence view favored by Druault, Ladd-Franklin, and Judd.

[7] The writer is indebted to Dr. Judd for various suggestions regarding this study and manuscript.

[8] This refers to the universal agreement on a characteristically present, dominant blue component, but the following list shows the variety in the subjective estimates actually reported by various investigators; purple, slightly reddish-blue, pale reddish-blue, blue to purple variation, violet, blue-violet, whitish-violet, blue, reasonably pure blue, whitish-blue, matt light blue.

[9] This result was for a range of retinal illuminations from 5 to 640 photons. Nearer the threshold, however, the arcs appear to increase in brilliance with increase in stimulus. Cf. H. Gertz, Hubbard, Ellis, Judd, and Snell.

[10] The several estimates of duration average somewhat less than 1 second. H. Gertz's estimate was 0.75 to 1.0; Troland's 1.0; and Snell's 0.8 sec.

out an element heretofore ignored, perhaps because lacking in adjustment value.

Unfortunately, a third condition of the occurrence of the arcs, one which had been asserted by H. Gertz, Druault and Amberson but more recently denied by Friedman, was not understood soon enough to affect the design of the main experiment. This condition is the degree of light and dark adaptation, a factor meriting special quantitative study. But data at hand suffice to establish the qualitative fact that brilliant arcs depend on relatively limited exposure to darkness. Insufficient control of this unexpected relation could account for large differences in brilliance determinations.

The color of the obtained arcs was measured by matching to them the known additive mixture of a special trichromatic colorimeter.[11] The observer is requested to fixate the comparison field and to match the arcs for hue, brilliance, and saturation. Then the stimulus is presented, the arcs appear, and in successive trials the mixture is progressively approximated to them until at length the match is made and an equality judgment can be reported. The mixture is adjusted between, rather than during, the brief observing periods, the task of the observer during those periods being limited to the observation of the simultaneously present arcs and mixture and to the formation of the judgment of equality or difference.

The characteristics of the observational field employed are indicated in Fig. 1. The vertical strip stimulus, S, is 0.5° by 6° angular size while the comparison field or mixture, M, is 2°. The 20° surrounding field or projection ground is adjustable in brightness. Except as otherwise stated, this brightness was approximately 0.005 ml, the equivalent retinal illumination in Troland's original unit being 0.07 photon.[12] An estimate was also made of the chromaticity of the ground. This was done by raising its illumination as far as possible without altering the quality of the light from the illuminant, and then adjusting the mixture to match it. The I.C.I. trilinear coordinates based on 10 trials were, $x=0.49$, $y=0.38$, $z=0.13$. Reference to the mixture diagram shows

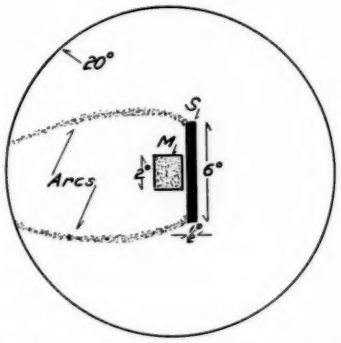

FIG. 1. The observational field with the projection of the blue arcs of the left eye.

that this determination is not far from 2360°K on the Planckian locus. The ground did not, however, appear particularly yellowish under the low level illumination of the experiment. When an observer fixated appropriately with his left eye near the middle of area, M, presentation of the stimulus would be accompanied normally by arcs projected to the relative size and shape shown.[13]

The observer viewed the field described above through an artificial pupil. His head was supported by a rest within a black hood which shielded him from the stray light escaping from the experimenter's scale-reading lamp and the colorimeter lamp housings into the otherwise dark room. The procedural detail was as follows: While fixating the comparison area, M, the observer depresses a key with his left hand which exposes the mixture in M, and with his right hand presses a time shutter control which exposes the stimulus light for 0.5 second. The arcs appear with the stimulus and are compared with the mixture, comparison being confined to arc segments above and below M rather than close to S. The observer reports the nature of any disparity between the colors of the arcs and mixture and the experimenter, or in some cases the observer himself adjusts the mixture to reduce the disparity. Then another trial is made followed by

[11] S. M. Newhall, Psychol. Monog. **47**, 199 (1936).

[12] L. T. Troland, Psych. Rev. **22**, 167 (1915), and J. Exper. Psych. **2**, 1 (1917).

[13] Beyond the field, these arcs accurately converge toward, and sometimes seem to join at, the projected papilla. Subject H regularly reported that the arcs joined and he was trained in the introspective school. Incidentally, if the juncture is real and at the correct angular distance from the fovea, there is here definite evidence for vision in the blind spot.

further adjustment. This process is continued until the mixture appears to the subject to match the arcs. Then the experimenter reads and records the three scale settings showing the amounts of the instrumental primaries in the matching mixture. This completes the experimentation for one determination. Occasionally the room light was turned on and the observer was permitted to remove his head from the hood to rest and reinforce the arcs. The mean of 10 or 20 determinations was taken as representative for a given observer under given stimulus conditions. These match data in terms of the instrument were transformed to the I.C.I. standard coordinate system with equal energy as basic stimulus.[14]

Since the technical problems of entoptic colorimetry are numerous as well as new they will be given detailed consideration elsewhere. But the extent to which the present data fulfill a fundamental requirement of all colorimetry must be considered here. This is the requirement of a satisfactory match of the given sample. Failures of the following four types were occasionally reported: (1) a volumic or tridimensional character in the arcs not reproducible with the matching mixture; (2) a texture or grain in the arcs not present in the mixture; (3) a saturation of the arcs too great to match directly; and (4) a momentary darkening of the comparison field simultaneous with the primary stimulus and interfering with the match. These difficulties were not regarded sufficiently prominent or frequent to vitiate present results; but they undoubtedly had

TABLE I. *The arcs vs. the stimulus in I.C.I. trilinear coordinates, x, y, z. n=20.*

	R			*Y*			*A*			*G*			*B*		
STIM.	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
	0.636	0.342	0.022	0.551	0.409	0.040	0.452	0.392	0.156	0.390	0.533	0.077	0.177	0.055	0.768
ARCS															
D	.230	.102	.668	.239	.123	.638	.223	.127	.650	.218	.167	.614	.183	.067	.750
F	.353	.129	.518	.342	.138	.520	.293	.105	.602	.278	.139	.583	.201	.067	.732
H	.257	.102	.641	.271	.110	.619	.265	.118	.617	.230	.090	.680	.229	.089	.682
N	.287	.112	.601	.265	.108	.627	.262	.115	.623	.248	.096	.656	.204	.073	.723
P	.248	.121	.631	.243	.102	.655	.267	.152	.581	.249	.113	.638	.215	.091	.694
M	.275	.113	.612	.272	.116	.612	.262	.123	.615	.245	.121	.634	.206	.077	.716

TABLE II. *Possible variations of measures of arcs and stimulus in I.C.I. trilinear coordinates, x, y, z.*

	R			*Y*			*A*			*G*			*B*		
STIM.	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
	0.002	0.002	0.000	0.000	0.000	0.000	0.003	0.003	0.006	0.001	0.001	0.000	0.000	0.000	0.000
ARCS															
D	.014	.024	.037	.013	.026	.038	.023	.041	.064	.020	.049	.069	.018	.019	.037
F	.005	.005	.000	.018	.001	.028	.006	.001	.007	.004	.029	.026	.016	.008	.024
H	.000	.004	.005	.011	.014	.026	.010	.008	.002	.012	.010	.022	.002	.001	.001
N	.009	.006	.015	.008	.005	.013	.008	.010	.017	.010	.005	.015	.003	.004	.008
P	.041	.016	.056	.029	.018	.047	.030	.025	.055	.029	.017	.045	.023	.052	.075
T	.020	.007	.027	.009	.011	.019	.006	.008	.015	.007	.015	.022	.004	.004	.007

TABLE III. *The arcs vs. the stimulus in dominant wave-length* λ, *Troland's photon, I, and spectral excitation purity, P. n = 100.*

	λ	*I*	*P*	λ	*I*	*P*	λ	*I*	*P*	λ	*I*	*P*	λ	*I*	*P*
Stim.	607	242	.93	591	192	.88	587	151	.54	565	72	.77	450	22	.89
Arcs	564*c*	.76	.76	565*c*	.68	.74	566*c*	.80	.70	568*c*	.76	.67	570*c*	.44	.78

[14] D. B. Judd, J. O. S. A. **23**, 359 (1933).

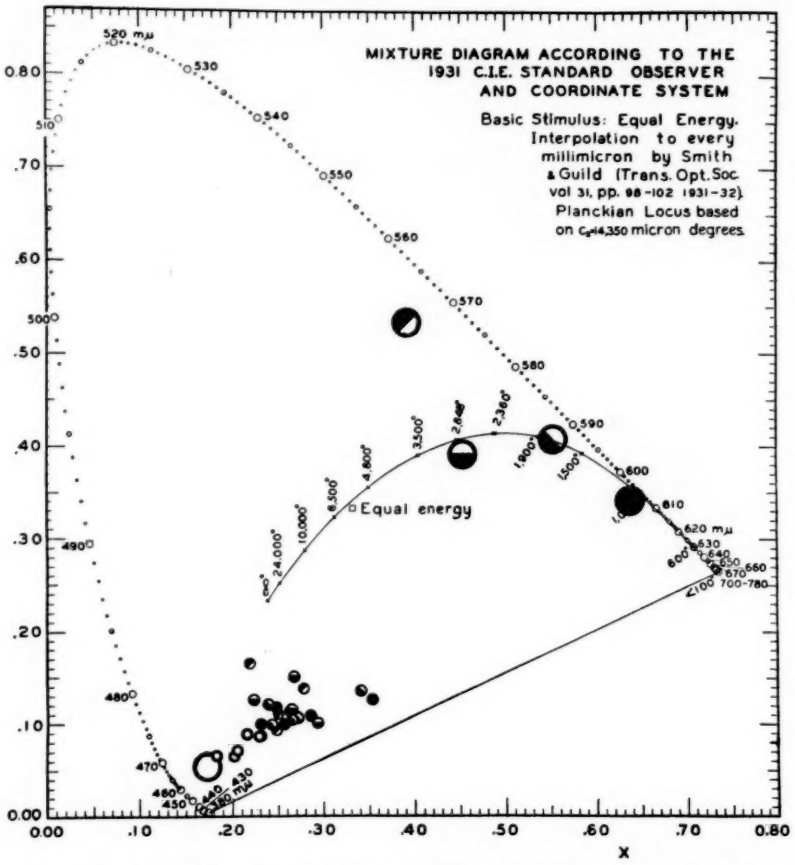

FIG. 2. The chromaticity of the arcs, small circles, and their stimuli, large circles, as plotted in the I.C.I. mixture diagram from the data of Table I.

some influence, and with other entoptic phenomena the third difficulty in particular might prove to be formidable.

INFLUENCE OF CHROMATICITY OF STIMULUS

The chromaticity data in Table I are for five different stimuli and for the arcs of five observers as elicited by each of those stimuli under the conditions above given. Each of the 25 sets of I.C.I. trilinear coordinates for the arcs is based on 20 determinations, each mean value in the bottom row representing 100 determinations. The photon value of each stimulus was chosen by trial to lie in the optimum range for brilliant arcs.

A comparison of the ranges of the trilinear coordinates of arcs and stimuli will show a relative constancy of the arcs and an independence of the arcs with respect to the stimuli. While the coordinates (x, y) of the stimuli range from (0.636, 0.342) to (0.177, 0.055), the coordinates of the corresponding mean arcs range only from (0.275, 0.113) to (0.206, 0.077). Separate figures for dominant wave-length and spectral excitation purity may be taken from Table III, as follows: for the stimuli, 607 mμ and 0.54 to 450 mμ and 0.93, and for the arcs, 564c mμ and 0.67 to 570c mμ and 0.78.[15] This conversion was made by the standard methods developed by Priest and Judd, and by the use of Klughardt's ratio principle in

[15] A wave-length number ending with a small c is the complementary of the matching color. This convention has been used regularly in the wave-length specification of the arcs because the arcs usually fall in the purple.

the purple as well as in the spectral region.[16] Evidently gross variation in the chromaticity of the stimulus was accompanied by relatively small variation in the chromaticity of the arcs.

Though the variability of the arcs is certainly small relative to the stimulus, the approximate uncertainties or possible variations in Table II indicate that this variability exceeds chance expectation.[17] The bottom row of the table gives the variations for the total cases in each column. Fig. 2 graphically represents the dispersion, ascribable to both experimental error and individual differences, of the 25 values set forth in the body of Table I. The arcs are seen to swarm near the violet-purple corner of the I.C.I. real chromaticity space, and from close inspection it again appears that the scatter is not entirely accidental.

The scatter is analyzed with respect to the chromaticity of the stimuli by plotting the coordinates of the mean arcs against the coordinates of the corresponding stimuli, as shown in Fig. 3. The slopes of the curves demonstrate a moderate plus dependency between the coordinates of arcs and stimuli. Table III, however, shows a rank difference correlation of -1.00 between the dominant wave-lengths of the complementaries of the arcs and the dominant wave-lengths of the respective stimuli. This suggests that the dependency is more a matter of hue and less of saturation. It agrees with Snell's observation that the arcs appear redder with long wave stimuli and bluer with short wave.

Influence of the chromaticity of the stimulus on the *brilliance* of the arcs was not evident except in case of the shortest wave-length stimulus. Specifically, Table III shows that with stimuli ranging from 607 mμ to 565 mμ the brilliance of the arcs ranged randomly from only 0.68 to 0.80 foveal photon; but with stimulus 450 mμ the brilliance of the arcs averaged only 0.44 foveal photon.[18] In view of the fact that maximum brilliance determinations have only been around 0.9 photons, the above is a marked difference and reaffirms the fact that a blue or violet stimulus elicits feeble arcs. All of our subjects reported difficulty in getting "good" arcs with the 450 mμ stimulus. Both Ellis and Snell even reported that no arcs were visible with a violet stimulus.

Influence of Retinal Illumination of Stimulus

Throughout this series on the influence of retinal illumination, the projection ground was dark, the stimulus employed was the "*A*" stimulus with coordinates $x=0.452$, $y=0.392$, and there was only one observer.

The psychophysical threshold of the arcs was determined by the method of constant stimuli. The first row of Table IV shows the constant stimulus intensities in terms of retinal illumination or photons and the second the resulting relative frequencies of reported perception of arcs. The relative frequencies of occurrences of chromatic arcs as distinct from those reported gray, are given in the bottom row. The absolute threshold, regardless of color, was computed from the

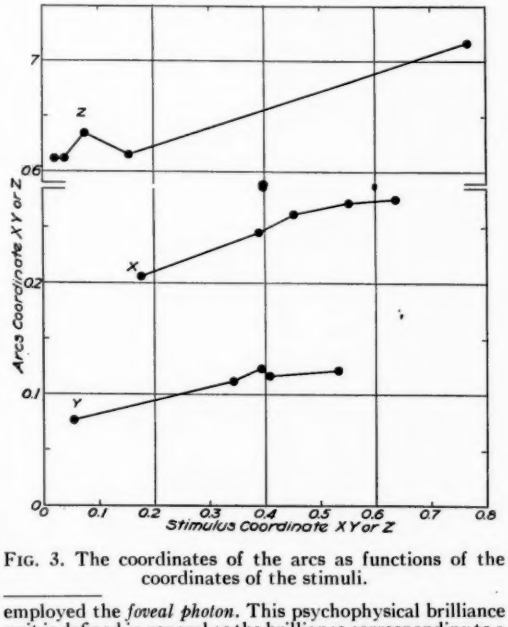

FIG. 3. The coordinates of the arcs as functions of the coordinates of the stimuli.

[16] D. B. Judd, Nat. Bur. Stand. J. Research **7**, 827 (1931). D. B. Judd, J. O. S. A. **23**, 359 (1933). A. Klughardt, Zeits. f. tech. Physik **10**, 101 (1929).

[17] The measure of the "possible variation" is three times the standard error, i.e. 3 σ_m, which includes virtually the entire effective range for statistically normal data.

[18] Since the relation between retinal illumination and brilliance varies enormously with the region stimulated, the photon or unit of retinal illumination cannot be used even as a relative measure of brilliance when comparing different regions. For that purpose we have, therefore, employed the *foveal photon*. This psychophysical brilliance unit is defined in general as the brilliance corresponding to a foveal, or at least macular, stimulus of 1 photon.

TABLE IV. *Relative frequency of the arcs vs. the photon value of the A stimulus near the absolute threshold. n=40. Subject N.*

A STIMULUS, *I*	0.4	0.8	1.6	2.4	3.2	4.0	4.8	5.6
Rel. freq., total	0.025	0.150	0.400	0.525	0.825	0.900	0.850	0.925
Rel. freq., hueful					0.075	0.200	0.175	0.400

data in the first and second rows by the abbreviated constant process and found to be 2.11 photons with a possible variation of 0.72 photon.[19] This result is intermediate with respect to previous estimates by Troland and Judd.

An estimate was made of the brilliance of the threshold arcs themselves and this was found to be of the order of 0.004 foveal photon which is, interestingly enough, of the same order as the absolute sensory threshold of primary stimulation.[20] The data of this estimate are represented by the plotted points at the left end of the curve in Fig. 5. The only previous data bearing on this result are in essential agreement with it.[21]

The observer's reports agree with Judd in calling the threshold arcs achromatic, but they occasionally exhibit hue slightly above the threshold, and do so increasingly with increase in retinal illumination. These facts are evident from Tables IV and V.

A more complete relationship between hue of arcs and retinal illumination was sought by varying the stimulus from near threshold to 10,000 times threshold with instruction to report hue or lack of hue of the arcs. The results of this experiment are shown in Table V. While the frequencies of report in the body of the table refer to 10 exposures at each stimulus value, there were sometimes more than 10 because of failure to elicit the arcs in 10 successive trials. That was inevitably the case near the threshold. The symbols heading the frequency columns and indicating the reported hues, mean, respectively: gray, reddish-gray, yellowish-gray, bluish-gray, blue, violet, purple. Of course, this type of report is difficult and subject to error. The reddish-gray and yellowish-gray reports are so few as to be suspect. While reports of gray are found at the extremes, reports of blue, violet, or purple, preponderate in the long middle range. The latter also show the highest total frequencies in the bottom row of the table.

While the subjective estimates in Table V certainly give some idea of how the arcs appeared at different stimulus levels, it seemed worthwhile to attempt actually to match the arcs at different intensities. Fig. 4 shows the result of measuring the arcs throughout the entire range in which trichromatic colorimetry seemed at all useful, i.e., from 15 to 5500 photons. Each plotted point represents 10 matches. As a basis of reference the left margin of the figure has been made to coin-

TABLE V. *The reported hue of the arcs vs. the A stimulus in photons, I, and relative to the absolute threshold of the arcs, RL. n=10. Subject N.*

A STIMULUS		REPORTED HUE						
I	*I/RL*	*gy*	*Rgy*	*Ygy*	*Bgy*	*B*	*V*	*P*
2.2	1.04	8		1	1			
4.9	2.3	6		1	2	1		
6.0	2.8	7			1	1		1
7.6	3.6	3			6	1		
9.2	4.4				6	2	1	1
15	7.1	1			5	2		2
22	10	2			1	2	2	3
63	30						2	8
130	62					1	2	7
170	81				1		5	4
400	190					3	4	3
600	280					2	3	5
1000	470					2	5	3
1500	710						5	5
2300	1100					2	4	4
3900	1900					8	1	1
5500	2600				1	7		2
10000	4700	1	1		1	6		1
15000	6200		1		2	4		3
21000	10000	2		2	3	2		1
Total		30	2	4	30	46	34	54

[19] S. M. Newhall, Psych. Rev. **35**, 46 (1928).

[20] D. M. Purdy, Brit. J. Psych. gen. sec. **21**, 283 (1931). S. M. Newhall and R. R. Sears, Comp. Psych. Monogs. **9**, 1 (1933).

[21] Troland not only observed that his arcs were regularly very weak but also showed experimentally that their brilliance exceeded but slightly the brilliance of primary threshold stimulation. The entire brilliance range of his arcs was given as approximately 0.0009 to 0.0031 photon which is below our threshold brilliance and below representative threshold brilliance values for primary foveal stimulation. This discrepancy might be due to difference in instrumentation, sensibility, or the fact that Troland's comparison field was approximately the same distance from the projected fovea as was his matched arc. Therefore his match was in terms of a "peripheral" photon whereas ours was in terms of a foveal photon. A brilliance standard from a photon falling on a peripheral area would necessarily yield a numerically lower brilliance determination than the foveal match. Thus the different brilliance reported might be due to the different brilliance unit employed.

cide with the locus of the absolute arc threshold for the "*A*" stimulus.

The high *z* curve and the lack of definite trend away from the horizontal of any of the coordinate curves in Fig. 4 confirm the preponderance of purple, violet, and blue verbal judgments in Table V. With the range of retinal illuminations from 15 to 5500 photons, the range of dominant wave-lengths of the arcs was only 568*c* to 571*c* mμ, and the range of excitation purities of the arcs only 0.81 to 0.86. Evidently, wide variation in the retinal illumination was accompanied by relatively small variation in the chromaticity of the arcs. In other words, the chromaticity of the arcs appears to be largely independent of illumination over a considerable range of retinal illumination.[8]

Around the absolute threshold there was obvious evidence of a functional relationship between the brilliance of the arcs and the retinal illumination of the stimulus. Fig. 5 represents an attempt to trace the brilliance of the arcs throughout the range of illuminations from threshold to 21,000 photons at which point observation had become exceedingly difficult. Each plotted point represents the mean of 10 trials. The values below 15 and above 5500 photons are the most uncertain because of the difficulty of satisfactorily matching; but those within that range were computed from the same colorimetric data as Fig. 4. The relatively low values at the extremes of this log brilliance curve are statistically significant, but so is the marked dip in the middle range. The figure indicates that arcs elicited by either near-threshold or relatively intense stimuli are low in brilliance, whereas arcs elicited by stimuli within a long intermediate range are of relatively high brilliance.[9]

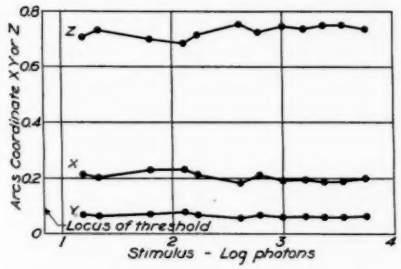

FIG. 4. The coordinates of the arcs as functions of the retinal illumination of the "*A*" stimulus.

INFLUENCE OF DURATION OF STIMULUS

The observers as well as several visitors were requested to compare the duration of the arcs with the duration of the stimulus. Sometimes the stimulus was presented by the experimenter and sometimes by the subject himself. There was general agreement with respect to onset; both stimulus and response seemed to appear simultaneously. When the stimulus was less than a certain critical duration the arcs usually appeared also to terminate in coincidence with the stimulus, or more strictly, the primary image. There were several instances, however, in which the arcs appeared to lag slightly, disappearing a little later than the stimulus. Since it was believed that this lag might be due to attention being concentrated on the going off of the arcs, subjects who reported lag were instructed to try concentrating on the going off of the stimulus. Under those conditions lag was rarely reported.

The duration of the stimulus was systematically varied from 0.02 to 0.50 second for three observers with instruction to note any durational disparities of stimulus and arcs. The "*R*" stimulus ($x=0.636$, $y=0.342$), against the light projection ground, was used in this series. Again, a slight lag was occasionally reported, particularly at lower illuminations, but regardless of stimulus duration or intensity, there appeared no latency. Still H. Gertz, using an ingenious movement technique had reported a "very small" latency. Perhaps on the whole it may be said that the arcs appear to parallel quite closely the primary image in time.

When the stimulus exceeded the critical value of the order of 0.9 second the arcs were observed to have disappeared independently. This maximum duration of the arcs was measured chronoscopically by means of a hand-key operated by the observer. The key was closed, starting the chronoscope, as soon as possible on seeing the arcs appear, and was released, stopping the chronoscope, as soon as the arcs were observed to disappear. A balanced series with four observers was arranged to show not only representative values for the duration but also the possible influence of the projection ground or the stimulus

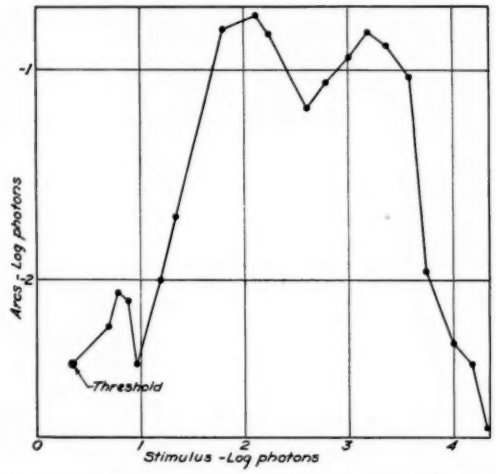

FIG. 5. The log brilliance of the arcs as a function of the log retinal illumination of the stimulus.

illumination on the duration. Table VI gives the values secured for each observer under the eight different conditions.

The means in the bottom row indicate that varying the stimulus from 35 to 1750 photons produced no marked change in the duration of the arcs. The maximum mean duration, however, did occur under both ground conditions at 175 photons. The latter lies in the optimum range and suggests that if a greater stimulus range had been chosen a significant falling off at both ends might have been found. When the projection ground was light the arcs endured 0.765 second but when the ground was dark the arcs averaged 0.89 second. Thus it would appear that the duration is dependent on the projection ground. The fact that the luminous arcs merge with the illuminated ground more quickly than with darkness proves that there is a relatively gradual decline in brilliance during the final phase of the arcs. Perhaps the most representative single figure for the duration of the arcs is that with the dark ground, i.e., 0.89 second. This is confirmatory of earlier estimates.[10]

INFLUENCE OF PREEXPOSURE TO DARKNESS AND LIGHT

Increasing familiarity with the conditions of occurrence of the arcs made it increasingly evident that some major condition of their occurrence was passing unrecognized. Often, observers would report inability to see vivid or brilliant arcs, or that the arcs seemed particularly good at a certain time, or that they were much weaker toward the end of a session. When special care was taken to shield the observer from stray light, the arcs were particularly weak. Finally the discovery was made that the arcs regularly weaken in dark room series exceeding several minutes in length, and that marked recovery can be effected by subjection to general room light for a similar period. These facts were confirmed by varied incidental observations and by the qualitative series now to be described.

In this series the procedure was to bring the observer into the dark room in whatever condition of light adaptation he might then happen to be, to subject him to controlled durations of exposure to total darkness and to light from the incandescent lamp in the standard opal ceiling unit, and following such exposures, to test him for the presence and brilliance of the arcs. The observer was not required to colorimeter the arcs but merely to estimate the relative brilliance of the phenomenon on a 5-point subjective scale. The maximum of this scale was defined by the most prominent and striking arcs experienced

TABLE VI. *Measures of the duration of the arcs, with their possible variations in seconds, vs. the R stimulus in photons. n = 10.*

	Surround at 0.07 Photon				Surround at Zero			
Stim.	35	175	700	1750	35	175	700	1750
Arcs								
D	0.38(0.08)	0.43(0.02)	0.45(0.08)	0.57(0.23)	0.37(0.08)	0.35(0.02)	0.41(0.08)	0.73(0.27)
F	.75(.17)	.67(.08)	.73(.14)	.76(.13)	.75(.09)	.70(.11)	.77(.11)	.83(.11)
H	1.13(.07)	1.21(.30)	1.17(.21)	1.04(.11)	1.51(.22)	1.41(.23)	1.32(.25)	1.02(.17)
P	.77(.29)	.86(.25)	.67(.23)	.64(.14)	1.07(.37)	1.28(.30)	.91(.27)	.72(.25)
M	.76(.15)	.79(.16)	.76(.15)	.75(.15)	.93(.19)	.94(.22)	.85(.18)	.83(.20)

under favorable conditions by the given observer and the minimum by his feeblest, near-threshold arcs. The estimate of zero was permitted in cases in which all other requirements for the occurrence of the arcs appeared to be fulfilled, but in which they failed to appear.

The R stimulus ($x=0.636$, $y=0.342$) was set in the optimum range, and the projection ground was dark. Each of the four observers made 10 successive estimates under each of several prescribed conditions. These estimates on the 5-point scale were then converted to percent of maximum brilliance and are so recorded in Table VII. The first two rows show the minutes of dark or light adaptation employed, while the columns below indicate the estimated brilliance of the arcs immediately following such dark or light adaptation periods. These columns are paired to show those estimates, after darkness and light, which belong together. Paired estimates are comparable in the sense that they followed each other experimentally in the same session. The estimates in the last column were made after "indefinite" light adaptation followed by "minimum" dark adaptation. This means that as soon as feasible after the subject reached the laboratory and the room lights were turned off, experimentation commenced. The term "minimum" means an unknown fraction of one minute. There were, unavoidably, a few seconds of moderate dark adaptation at the start of every series of estimates. The table shows in general not only that exposure to prolonged darkness after light weakened the arcs but also that exposure to light after darkness strengthened them.

TABLE VII. *Subjective estimates, in percent of maximum, of the brilliance of the arcs following various exposures, in minutes, to darkness and light. n = 10.*

DARKNESS / LIGHT	60	5	30	5	15	5	10	5	5	5	MIN. INDEF.
OBSERVER											
D			32	74	18		20	86	18		98
F	0		32	68	32	78					76
H	0	74	20	68					32	54	74
P	2	42	8	46					20	54	86
M	1	58	23	64	25	78	20	86	23	54	84

DISCUSSION

Information has been secured concerning the two unsettled points noted at the outset, i.e., the nature of the secondary stimulation and the receptors for it. As might be expected a simple explanation has not been found.

With respect to the first point, there is (1) the fact that the arcs definitely weaken during adaptation to darkness even while the light threshold is falling, and this suggests that the secondary stimulus is not photic. If it were photic one would expect the arcs to strengthen with increasing light sensitivity. Whether the observed weakening can be correlated with some physiological change or vitamin variation remains to be seen. (2) Others have found that preliminary light stimulation sometimes raises the electrical excitability of the retina while subsequent darkness adaptation regularly depresses it.[22] We found that preliminary light stimulation raised the excitability of the eye for the arcs and that subsequent darkness regularly depressed it. The fact that the arcs and electrical thresholds thus vary together independently of the light threshold, strongly suggests that the secondary or immediate stimulus for the arcs is electrical. (3) Minimal lag or latency in the luminous phenomenon would also favor the electrical hypothesis because the sensory effects of electrical stimulation are commonly more rapid and less persistent than those of light stimulation. The present procedure on this point is not regarded sufficiently sensitive to be decisive.

Furthermore, most experienced observers do occasionally see the so-called negative after-image consisting of dark or black arcs against the less dark field. And, so far as the writer has been able to discover, not more than four observers have seen any other kind of after-image. Friedman reported a distinct colorless, positive after-image. The writer's subject *P* noticed once an unsaturated blue after-effect which developed into a whitish gray. Hans Gertz wrote of his results on two occasions. In 1907, he described a very fleeting, pale grayish-yellow after-image of the Neuroaktionsphosphen or arcs, but there is no definite assurance that any of his subjects

[22] G. E. Müller, *Ueber die Farbenempfindungen* (Leipzig, 1930), p. 370 and Zeits. f. Sinnesphysiol. **65**, 282 (1934). J. D. Achelis and J. Merkulow, Zeits. f. Sinnesphysiol. **60**, 95 (1930). F. P. Fischer and K. vom Hofe, Arch. f. Augenheilk. **105**, 443 (1932). A. Bogoslovsky, S. Kravkov, and E. Semenovskaya, Fiziol. Zh., U. S. S. R., 814 (1935). A. I. Bogoslovsky, v. Graefes Arch. Ophthal., **133**, 105 (1935).

saw it. In 1909, after special study of the after-image, Gertz reported that he had discovered optimal conditions and secured unmistakable results. The image then observed was described as directly following the arcs themselves and as being a gradually fading trace of dark streaks which looked like black velvet on the gray ground. "Whether or not this after-image has color I have not been able to definitely decide." Under the most favorable conditions Gertz thought he observed along the edges of the streaks an extremely faint brownish coloration, perhaps a touch of rust brown. Ladd-Franklin, the fourth observer referred to above, reported a chromatic after-image of dark olive or yellow-green hue, but that may have been a reference to Gertz rather than to personal observation.

Ladd-Franklin's important argument for the bioluminescence view was that the blue arcs are followed by a complementary chromatic after-image, the latter being inducible by light but not by electricity. This argument now seems untenable because of evident doubt regarding the sensory fact upon which it was based. Only Gertz's admittedly uncertain result and the report of Ladd-Franklin herself could possibly fulfill the requirements.

On the other hand, it seems noteworthy that an after-effect, whether chromatic or merely dark, might be electrically initiated after all. As Davis pointed out, even though an externally applied electrical stimulus might give no after-image, an internally arising electrical disturbance like a retinal action current might stimulate the photosensory mechanism.[23] Such a secondary electrical stimulus occasionally modifying the receptive substance and so providing the necessary occasional basis for an after-image, would seem consistent with Müller's view of electrical retinal excitation.[24] If the meager evidence for chromatic after-arcs can be ignored, even the insistence that the sense-cells must be modified by the arc stimulus, may be superfluous. The fact that receiving fibers lying along the arc courses have been highly active while those in the surrounding field have not, suggests that some fatigue differential might still account for the contrast between the dark after-arcs and the less dark projection ground. Ellis even went so far as to state that there is no true after-image of the arcs to be accounted for, and that the apparent dark after-arcs are merely defects in a faint after-image of the diffuse blue haze.

(4) The fact that the arcs accompany the primary image harmonizes with the buzzer, membrane, and volley hypotheses of sensory neural activity and, in that sense, favors the electrical view of the arcs. It will be easiest to show how this is so by indicating the principal implications of these hypotheses for the phenomenon. On the buzzer hypothesis, the primary stimulus induces a periodic activity in the receptor which determines the rate of discharge in the connected fiber. On the membrane hypothesis, there is a periodic electrical change about excited fibers which corcorresponds exactly to the flow of impulses "through" them. On the volley principle, the rhythmic discharge in parallel fibers may be synchronized. Taken together, these implications evidently harmonize with the idea of a relatively strong, periodic, electrical flux in the immediate vicinity of the closely packed papillo-macular fibers, of sufficient intensity to pass the thresholds of sensitive elements along their courses, and so give rise to the observed phenomenon. The periodic discharge, like interrupted current in general, would serve as an enduring secondary stimulus, and the luminous arcs would parallel the primary image in time because both would depend directly upon the activity of this primary discharge.

The remarkably regular disappearance of the arcs after about 0.9 second seems equally agreeable to electric or photic theory. Three conceivable interpretations may be merely mentioned. The adaptational fall in the primary excitation might render the relatively weak arc stimulus subthreshold in about 0.9 second; or the arc stimulus might fall below a rising threshold in its own receiving elements; or those secondarily excited fibers might themselves go into belated refractory phase in the same period of time.

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[23] Of interest in this connection is the fact that chromatic effects from externally applied electrical stimuli *have* been reported in which the hue has been called violet or greenish-yellow according to the direction of the flow of the current. H. Gertz, in the 1909 paper, has cited such electrical complementary effects as a basis for explaining the alleged chromatic after-arcs. He reported that the complementary sensation would arise when the extrinsic current was merely cut off.

[24] G. E. Müller, Zeits. f. Sinnesphysiol. **65**, 274 (1934).

Concerning the second unsettled point, i.e., the receptors of the secondary stimulation, the form of the phenomenon certainly indicates that they lie along the paths of the fiber bundles. Otherwise, as Ladd-Franklin pointed out, the place coefficients would be incorrect. This does not serve to identify the secondary receptors themselves but that may be attempted by inference from the observed colors of the arcs. These having been variously reported as gray, blue, violet, and even purple, the inference is that achromatic, violet, and possibly red receptors are severally involved. If the several receptors differed in their sensitivity for the electrical arc stimulus, as they do for the normal light stimulus,[25] then the color of the arcs should vary with the intensity of the arc stimulus. The latter intensity would itself depend upon the primary light stimulus and the unexplained influence of dark adaptation.

(1) The gray arcs observed at the threshold support the view that achromatic, rod receptors are most sensitive to the arc stimulus. The minimal arcs seen after prolonged dark adaptation are believed to be gray for the same reason. The pale bluish arcs usually observed slightly above the threshold would be due to combined achromatic and violet reception. The definitely violet hue at somewhat higher levels could be ascribed to greater activity of violet receptors. So far, then, differential sensitivity of achromatic and violet receptors could account for the observations.

(2) But the purplish arcs often seen at optimal illuminations with long wave light and limited dark adaptation, may possess a red component beyond that attributable to the violet system. If they do the red system must also be activated. This activation would probably be by stray red light within the eyeball. This photically stimulated red would have to combine centrally with the electrically stimulated violet to yield the observed purple phenomenon. Indeed, there would seem to be no other way of interpreting the experimental result in Table III that the hue of the arcs is correlated with the hue of the stimulus.

(3) The longer wave primary stimuli are the more favorable to the occurrence of the arcs partly perhaps because the achromatic and violet receptors are relatively insensitive to long wave stimuli. Therefore, stray light from such stimuli would interfere relatively little with that secondary electrical stimulation of the achromatic and violet receptors which is believed to be the chief basis of the blue arc phenomenon.[26] There is also some possibility that the longer wave stimuli may be more favorable because they elicit more electrical response, i.e., more arc stimulus.

(4) The striking though imperfect constancy of the phenomenon with respect to both hue and brilliance may be interpreted tentatively. The blue component is believed to predominate regularly on the assumption that achromatic and violet receptors are the most sensitive to the arc stimulus and the latter is incapable of exciting the other less sensitive receptors. The brilliance of the arcs is believed to remain somewhere near the same level through a considerable range of retinal illuminations because of the balancing effect of two opposing factors. The first is the intensity of the arc stimulus and the second is interference by stray light with the sensitive receptors of the arc stimulus. Both vary with the primary light stimulus. At low, near-threshold stimulation the first factor would predominate and the arcs would increase in brilliance with increase in primary stimulus. At high, superoptimal levels, the second factor would dominate and the arcs would fall off.

Summary

1. The blue arc phenomenon is closely dependent upon the retinal area stimulated, the direction of attention attained, and the state of adaptation present.

2. The phenomenon is relatively independent of large variations in the color of the inducing stimulus, but there is a limited dependency of hue of arcs on hue of stimulus.

[25] Apart from the general implications of the duplicity principle and the Purkinje phenomenon, there are various specific indications of a high sensitivity of violet or blue receptors at scotopic or low levels of illumination. A. König, Sitz. d. preuss Akad. d. Wissenschaft, Phys.-math., 577 (1894). J. v. Kries and W. Nagel. Zeits. f. Psychol. **12**, 1 (1896). W. Nagel, Zeits. f. Sinnesphysiol. **44**, 5 (1909). V. O. Siven, Arch. Ophthal. **42**, 156 (1913). O. Kroh. Zeits. f. Sinnesphysiol, **53**, 187 (1921). M. Tscherning, Ann. d'ocul. **159**, 632 (1922). H. v. Helmholtz, Physiol. Optics. O. S. A. trans. II, 347 (1924). H. E. Roaf, *Discussion on Vision*, Physical Soc. Pub., 316 (1932).

[26] At the arc threshold, where stray light is at a minimum, Judd even found short wave stimuli to be more effective than long wave.

3. Relatively long wave stimuli, e.g. 607 to 565 mμ, are definitely favorable to the occurrence of the arcs.

4. The color of typical arcs is a reddish blue, corresponding approximately to dominant wavelength 566*c* mμ, brilliance 0.75 foveal photon, and excitation purity 75 percent.

5. The arcs exhibit neither an appreciable degree of lag nor of latency; but if the stimulus is continued they disappear independently in approximately 0.9 second.

6. The arcs are achromatic at the absolute threshold of retinal illumination but rapidly increase in saturation and brilliance above it.

7. The brilliance of threshold arcs is of the order of 0.004 foveal photon which is the same as the sensory threshold of a primary light stimulus. The upper limit of the brilliance range of the phenomenon is around 0.9 foveal photon.

8. The value of the absolute threshold of the arcs in terms of the primary "*A*" stimulus was, for one subject, 2.11 photons with a possible variation of 0.72 photon.

9. Preexposure of the retina to light strengthens the blue arc phenomenon while prolonged exposure to darkness weakens it.

10. On the theoretical side these results favor, (1) electricity as the principal immediate stimulus for the arcs and, (2) both achromatic and violet elements as the receptors of that stimulation. The typical reddish cast of the arcs is at least partly ascribable to the violet receptors and may be partly due to stray light stimulation of the red cones.